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Thermal Properties of Copper(II) Chelates of Some 1,5-Alkylpentane-2,4-diones[1]

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Thermally stable and low melting copper(II) chelates of β-diketones have been synthesized as follows; bis(heptane-2,4-dionato)copper(II), mp 172°C; bis(nonane-4,6-dionato)copper(II), mp 162°C; bis(5-ethylheptane-2,4-dionato)copper(II), mp 72°C; bis(3-ethylnonane-4,6-dionato)copper(II), mp 50°C; bis(3,7-diethylnonane-4,6-dionato)copper(II), mp 58°C. Their thermal characteristics including enthalpy and entropy of fusion, have been discussed in relation with the molecular structure of the copper chelates.

In relation to our research project on the application of zone-melting technique to the systems containing metal chelate compounds,[2-6] we have been interested in the metal chelates which melt at relatively low temperature without decomposition. It has been known that the introduction of alkyl groups on 1 and/or 5 positions of 2,4-pentanedione results in the lowering of melting point of the corresponding metal chelates.[7-10] However, no systematic investigation on this respect have been appeared in literatures. This paper is to report on the results of the investigation on the thermal properties of copper(II) chelates of 1-

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[1] Contribution No. 250 from the Department of Organic Synthesis, Kyushu University.

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[3] K. Ueno, H. Kaneko, and Y. Watanabe, *Microchemical J.*, **10**, 244 (1966).

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[7] H. Gilman, R. G. Jones, E. Bindschadler, D. Blume, G. Karmas, G. A. Martin, Jr., J. F. Nobis, J. R. Thirtle, H. L. Yale, and F. A. Yoeman, *J. Amer. Chem. Soc.*, **78**, 2790 (1956).

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and/or 5-ethyl-substituted 2,4-pentanedione.

The ligands chosen in this study are heptane-2,4-dione (Etacac), nonane-4,6-dione (EtacacEt), 5-ethylheptane-2,4-dione (Et$_2$acac), 3-ethylnonane-4,6-dione (Et$_2$acacEt), 3,7-diethylnonane-4,6-dione (Et$_2$acacEt$_2$). The measurements of absorption spectra in visible as well as infrared region, the differential thermal analyses, the differential scanning calorimetric analyses, and the determination of melting point and molecular volume have been carried out on the 1:2 copper(II) chelates of the above ligands, and the relationship between the structure of the chelates and their thermal properties was discussed.

Experimental

Syntheses of Ligands. The ligands except Et$_2$acacEt and Et$_2$acac have been reported in the literatures, and they were synthesized by the condensation of corresponding ketone and ester in the presence of sodium amide. The ligands obtained were; Etacac (bp 67.5—70°C/20 mmHg),[11] EtacacEt (bp 101—102°C/20 mmHg),[8] and Et$_2$acacEt$_2$ (81—82°C/1.8—1.9 mmHg).[12]

The new ligands, Et$_2$acac and Et$_2$acacEt, were also synthesized in a similar manner to those described above, from 3-ethyl-2-pentanone and ethyl acetate for Et$_2$acac, and from 2-pentanone and phenyl 2-ethylbutyrate for Et$_2$acacEt. While the former was separated as pure ligand (bp 77°C/10 mmHg), the latter was not obtained as a pure form from the reaction mixture, and therefore the reaction product was directly converted into copper(II) chelate, which was eventually purified as copper chelate.

All these ligands were characterized in the form of copper(II) chelates by elemental analyses as shown in Table 1.

Preparation of Copper(II) Chelates. The copper(II) chelates of acac, Etacac, and EtacacEt were easily prepared by shaking stoichiometric amount of aqueous cupric acetate and the ligand, and the precipitated chelate was recrystallized from ethanol.

The copper(II) chelate of Et$_2$acac was prepared by the similar manner to the above procedure, but was obtained as dark violet oily product which crystallized after standing for a few hours. It was recrystallized from 80% ethanol to afford blue sticks. The chelate of Et$_2$acacEt$_2$, which was prepared by the similar manner, was also a dark violet oily product which slowly crystallized during 24 hours. If the ligand was not pure enough, the crystallization could hardly be observed. The crude chelate was recrystallized from 90% ethanol to afford blue sticks.

The copper(II) chelate of Et$_2$acacEt was prepared from the crude ligand and aqueous cupric acetate as described in the previous section. The crude copper chelate, which was obtained as a blue green oily product, was extracted with hexane. The hexane solution was washed successively with water and a saturated sodium bicarbonate solution. After evaporating hexane, blue oily residue was kept standing in a dish to afford a violet crystalline mass which was eventually purified by repeated precipitation from ethanol solution with water. No condition and solvent for the recrystallization of this chelate could be found.

Table 1. The molecular formula and the analytical results of the copper(II) chelates investigated

Chelate	Molecular formula	Elemental analysis			
		Found		Calcd	
		C%	H%	C%	H%
Cu(acac)$_2$	$C_{10}H_{14}O_4Cu$	45.89	5.63	45.91	5.35
Cu(Etacac)$_2$	$C_{14}H_{22}O_4Cu$	52.90	6.99	52.90	6.98
Cu(EtacacEt)$_2$	$C_{18}H_{30}O_4Cu$	57.82	8.17	57.81	8.09
Cu(Et$_2$acac)$_2$	$C_{18}H_{30}O_4Cu$	57.83	8.23	57.81	8.09
Cu(Et$_2$acacEt)$_2$	$C_{22}H_{38}O_4Cu$	61.21	8.89	61.44	8.91
Cu(Et$_2$acacEt$_2$)$_2$	$C_{26}H_{46}O_4Cu$	64.12	9.65	64.23	9.54

The molecular formula and the analytical data of the chelates are summarized in Table 1.

Apparatus and Procedure. Melting points were observed on a micro-hot-stage with a Yanagimoto micro melting point apparatus (model MP-S2) which was calibrated with a standard sample.

Densities of the copper(II) chelate were determined by the standard procedure using a 3—4 m*l* picnometer. The volume of immersion liquid displaced by a known weight of a finely powdered solid chelate was measured at 25±0.1°C. The molecular volume was then calculated by deviding the molecular weight by density. The result is summarized in Table 2.

The heat of fusion was determined with a Perkin-Elmer Model DSC-18 differential scanning calorimeter. The differential thermal analysis was carried out on a Rigakudenki Thermoflex-8001 with a 3—5 mg sample sealed in an aluminum capsule at a heating rate of 3°C/min, using alumina as a reference, either in air or in nitrogen atmosphere.

The thermodynamic characteristics of the copper(II) chelates are summarized in Table 3.

The infrared spectra were measured with a JASCO Model DS-403G grating spectrophotometer on the samples in KBr pellet, and the absorption spectra in visible region were measured with a Hitachi Model 124 recording spectrophotometer.

Results and discussion

DTA Study. In order to evaluate the thermal stability of the copper chelates, the differential thermal analysis (DTA) was carried out on the samples in air as well as in nitrogen atmosphere. The results are given in Fig. 1. The DTA curves except for Cu(acac)$_2$, are characterized with a sharp endothermic peak A. The endothermic peak (A) temperature was found to be in good agreement with the melting point of the respective copper chelate which was determined by the micro-hot-stage method (Table 3).

The repeated DTA measurement on the same sample up to the temperature 15°C above the melting point of the chelate, did not show any change of the endothermic temperature. This implies that the peak is not due to the decomposition, but purely due to the fusing process. This was also confirmed by the comparison of the infrared spectra of the samples before and after the DTA run, which were found to be exactly superimposable.

The samples of Cu(Etacac)$_2$, Cu(Et$_2$acacEt)$_2$, and Cu(Et$_2$acacEt$_2$)$_2$ did not show any change in the

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[11] R. Levine, J. A. Conroy, J. T. Adams, and C. R. Hauser, *J. Amer. Chem. Soc.*, **67**, 1510 (1945).

[12] E. H. Man, F. W. Swamer, and C. R. Hauser, *ibid.*, **73**, 901 (1951).

endothermic peak area and peak temperature as well as the sample weight during the repeated runs. On the other hand, Cu(Etacac)$_2$ decreased its sample weight and the peak area. The change can be ascribed to the slow sublimation or vaporization of the sample during the heating process.

As to Cu(Et$_2$acac)$_2$, a single endothermic peak at 71°C splitted into two peaks at 65°C and 70°C after the first run, however the sample weight and peak area remained constant during the repeated runs. As the twin peaks did not change after the second run, this may be related with a kind of phase transition accompanied with the fusing process.

The endothermic peak B at higher temperature in nitrogen atmosphere is related with the decomposition of the samples, while the complicated exothermic peaks in air at the same temperature range being related with the oxidative decomposition of the samples.

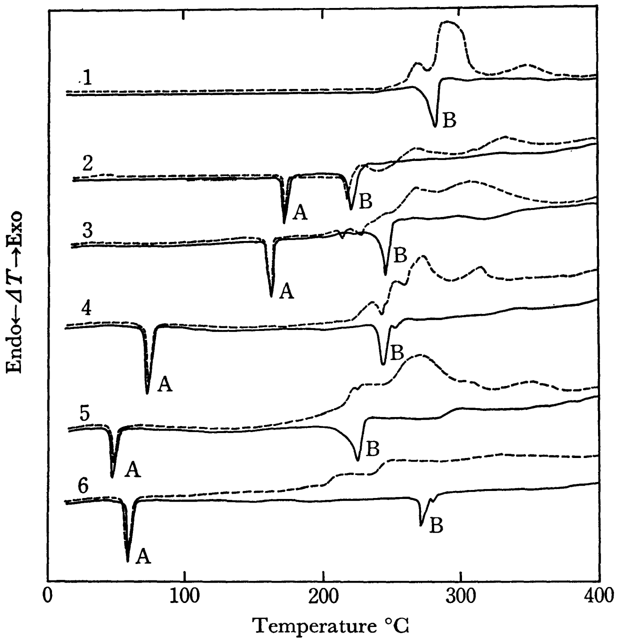

Fig. 1. DTA curves of the copper (II) chelates heated in nitrogen atmosphere (——) and in air (······).
1. Cu(acac)$_2$ 2. Cu(Etacac)$_2$ 3. Cu(EtacacEt)$_2$
4. Cu(Et$_2$acac)$_2$ 5. Cu(Et$_2$acacEt)$_2$ 6. Cu(Et$_2$acacEt$_2$)$_2$

The thermal stability of copper chelates, roughly estimated by the decomposition peak temperature, increases in the order of Cu(Et$_2$acacEt)$_2$<Cu(Etacac)$_2$ <Cu(Et$_2$acac)$_2$ <Cu(EtacacEt)$_2$ < Cu(Et$_2$acacEt$_2$)$_2$ < Cu(acac)$_2$. In general, the copper chelates of the symmetric ligands are more stable than those of the unsymmetric ligands, and the melting point becomes lower with increasing number of terminal ethyl groups on the ligand. Thus, the temperature range where the molten chelate is stable, is widest for Cu(Et$_2$acacEt$_2$)$_2$ and becomes narrower in the order of Cu(Et$_2$acacEt)$_2$, Cu(Et$_2$acac)$_2$, Cu(EtacacEt)$_2$, and Cu(Etacac)$_2$. Finally, the chelate of non-ethylated ligand, Cu(acac)$_2$, can not exist as molten state.

Spectral Study. As shwon in Table 4, the infrared absorption bands due to the stretching mode of C=C and C=O bonds in the chelate ring do not shift significantly from one chelate to another. The result suggests that the introduction of ethyl groups on 1 and/or 5 positions of pentane-2,4-dione does not affect appreciablly the bond strengths in the chelate ring of bis(pentane-2,4-dionato)copper(II).

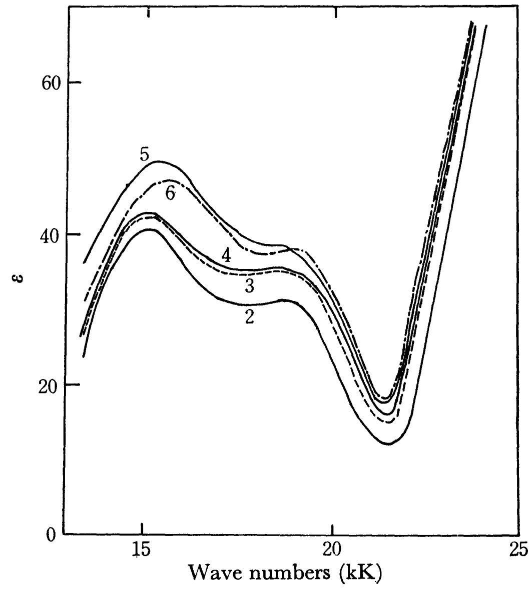

Fig. 2. Visible absorption spectra of copper(II) chelates in carbon tetrachloride at room temperature.
2. Cu(Etacac)$_2$ 3. Cu(EtacacEt)$_2$ 4. Cu(Et$_2$acac)$_2$
5. Cu(Et$_2$acacEt)$_2$ 6. Cu(Et$_2$acacEt$_2$)$_2$

The visible absorption spectra of the copper chelates in carbon tetrachloride are shown in Fig. 2. The spectra are characterized with two peaks at about 15000 cm^{-1} and 17500 cm^{-1} which shift very little with the kind of ligand, and the spectra are very similar to that of bis(pentane-2,4-dionato)copper(II) which is known to take a tetra-coordinate square planar structure. The similarity of visible absorption spectra regardless of the kind of ligands indicates that the introduction of ethyl groups on the terminal methyl carbon of the ligands does not cause any intramolecular steric hindrance which may results in the change in the symmetry of square planar coordination structute. The construction of molecular model also proved that the terminal ethyl groups did not cause any steric repulsion between the opposing two ligands in the chelate molecule. Furthermore, the molecular model suggested that the terminal ethyl groups fixed into rather restricted spaces with least steric interaction with the chelate ring, so that the ethyl groups could not rotate freely but extend above or below the x-y plane of the copper chelate.

The molecular volume of the chelate increases with the increasing number of ethyl groups introduced into the ligand as shown on the fourth column in Table 2. However, the increase of molecular volume per ethyl group increases as the complexity of the chelated ligand increases as indicated on the fifth column of Table 2. This tendency may be attributed to the mutual interaction of ethyl groups, as the increment should be unchanged if there is no interaction between the ethyl groups. As to the question of whether the interaction of ethyl groups is intramolecular one or

Table 2. Molecular volumes of copper(II) chelates

Copper chelate	Immersion liquid	Density d^{25}	Molecular volume V_M cm³/mol	Increase of molecular volume[a] ΔV_M cm³/mol	Increase of ΔV_M per ethyl group[b] cm³/mol
$Cu(acac)_2$	n-hexane	1.57	166.7	—	—
$Cu(Etacac)_2$	n-hexane	1.42	223.9	57.2	28.5
$Cu(EtacacEt)_2$	water-methanol	1.27	294.5	127.8	32.0
$Cu(Et_2acac)_2$	water-methanol	1.26	296.8	130.1	32.5
$Cu(Et_2acacEt_2)_2$	water-methanol	1.08	450.2	283.5	35.3

a) Increase of molecular volume of listed chelate from that of $Cu(acac)_2$.
b) Increase of molecular volume divided by the total number of ethyl groups introduced in the chelate molecule.

Table 3. Thermodynamic characteristics of copper(II) chelates

Copper chelate	Melting point °C	Melting point (T_f) °K	Enthalpy of fusion (ΔH_f) (kcal·mol^{-1})	Entropy of fusion (ΔS_f)[a] (e.u.)
$Cu(acac)_2$	263 (283)	536 (decomp.)	—	—
$Cu(Etacac)_2$	172 (170)	445	9.5	21.4
$Cu(EtacacEt)_2$	162 (162)	435	9.1	20.9
$Cu(Et_2acac)_2$	72 (71)	345	7.8	22.6
$Cu(Et_2acacEt)_2$	50 (45)	323	~6	~18.5
$Cu(Et_2acacEt_2)_2$	58 (57)	331	5.2	15.6

a) $\Delta S_f = \Delta H_f / T_f$
b) The values in parentheses were determined by the DTA study.

Table 4. Characteristic infrared absorption bands of the copper chelates

Copper chelate	Wave number of the band (cm^{-1}) -CH_3 ν_{C-H}	-CH_2- ν_{C-H} (as)	-CH_2- ν_{C-H} (s)	$\nu_{C=C}$	$\nu_{C=O}$	$\nu_{C=O}$
$Cu(acac)_2$	2969	—	—	1580	1554	1525
$Cu(Etacac)_2$	2966	2936	2876	1575	1552	1519
$Cu(EtacacEt)_2$	2966	2936	2876	1574	1549	1521
$Cu(Et_2acac)_2$	2968	2937	2879	1577	1552	1518
$Cu(Et_2acacEt)_2$	2966	2935	2876	1573	—	1518
$Cu(Et_2acacEt_2)_2$	2968	2938	2879	1576	—	1525

Table 5. Contribution of additional ethyl groups to the molecular volume

Difference in V_M between			ΔV_M/Ethyl group	Contribution from additional ethyl groups
$Cu(acac)_2$	-$Cu(Etacac)_2$	57.2	28.5	7.0
$Cu(Etacac)_2$	-$Cu(EtacacEt)_2$	70.6	35.5	
$Cu(acac)_2$	-$Cu(Et_2acac)_2$	130.1	32.5	5.8
$Cu(Et_2acac)_2$	-$Cu(Et_2acacEt_2)_2$	153.4	38.3	
$Cu(acac)_2$	-$Cu(EtacacEt)_2$	127.8	32.0	6.8
$Cu(EtacacEt)_2$	-$Cu(Et_2acacEt_2)_2$	155.7	38.8	

intermolecular one, the latter seems to be true from the following observations. First, there operates no steric interaction between the terminal ethyl groups within the ligand molecule or of opposing two ligands in the copper(II) chelate, as proved by the molecular model. Secondly, the extent of the contribution of additional ethyl groups to the increase of molecular volume of less complicated ligands remains almost the same as visualized in Table 5. If the interaction between the ethyl groups within the same ligand does exist, the value on the last column in Table 5 should increase with increasing degree of interaction. Additionally, molecular volume of $Cu(EtacacEt)_2$ and of $Cu(Et_2acac)_2$ are nearly equal (Table 2).

It has been shown that the visible absorption spectra of bis(pentane-2,4-dionato)copper(II) in chloroform (15000 cm^{-1} and 18000 cm^{-1}) changed into single band in pyridine (15200 cm^{-1}). According to Ortolano,[13] of the two absorption bands in chloroform, a band at 18000 cm^{-1} is assigned to a transition of d_{xy}—d_{z^2}. When the chelate is dissolved in a strongly coordinating solvent such as pyridine, this band receives a bathochromic and hypsochromic change and emerges into the parent band resulting in a broad band at 15200 cm^{-1} region, the reason for which is explained as the coordination of pyridine molecule to the central copper ion along the z-axis.

The similar spectral change was observed on the copper chelates investigated in this study, when they were dissolved in pyridine and in 2,6-lutidine. The results are summarized in Table 6. In contrast to

Table 6. Characteristic visible absorption bands of copper(II) chelates in various solvents

Copper chelate	Absorption bands in (cm^{-1}) Chloroform	Carbon tetrachloride	2,6-Lutidine	Pyridine	$\Delta\nu$[a]
$Cu(acac)_2$	15300	—	—	15200	—
	17800				
$Cu(Etacac)_2$	15200	15200	15200	15400	200
	—	18500			
$Cu(EtacacEt)_2$	15200	15100	15100	15400	300
	~18200	18500			
$Cu(Et_2acac)_2$	15200	15100	15000	15300	300
	18300	18500			
$Cu(Et_2acacEt)_2$	15200	15100	14900	15300	400
	18500	18600			
$Cu(Et_2acacEt_2)_2$	15200	15100	14500	15300	800
	18600	18700			

a) Difference of wave numbers between the absorption maxima in pyridine and in 2,6-lutidine.

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[13] L. L. Funck and T. R. Ortolano, *Inorg. Chem.*, **7**, 567 (1968).

the spectra in pyridine, where the frequency of absorption maxima remained almost unchanged for all chelates, those in 2,6-lutidine were broader in band width and showed rather wide variation in the frequencies. The latter spectra may be understood to be an intermediate stage of coordination of solvent molecule to the copper(II) ion, where the band due to d_{xy}—d_{z^2} transition does not completely emerge into the parent band, resulting in the broadening and the apparent bathochromic shift of the parent band. If it is the case, the extent of bathochromic shift of a bond near 15300 cm^{-1} in 2,6-lutidine from that in pyridine, can be used as a measure of estimating the intensity of interaction between the solvent molecules and the chelated copper(II) ion. In other words, the greater is the shift of the band between the two solvents, the weaker is the coordination of solvent molecules to the chelated copper(II) ion. As shown in Table 6, the order of decreasing intensity of interaction between 2,6-lutidine and the copper ion is $\text{Cu(Etacac)}_2 >$ Cu(EtacacEt) $>$ $\text{Cu(Et}_2\text{acac)}_2 >$ $\text{Cu(Et}_2\text{acacEt)}_2 >$ $\text{Cu(Et}_2\text{acacEt}_2)_2$. This order is in accordance with the shielding effect of ethyl groups introduced on 1- and/or 5-carbon of pentane-2,4-dione, if one assume that the terminal ethyl groups extend above or below of the *xy* plane of copper(II) chelate as discussed above.

Refering to the thermodynamic characteristics on the fusion of copper(II) chelates, it is noticed that the melting point of the chelate is dependent upon ΔH_f term rather than ΔS_f term. The monotonous decrease of the enthalpy of fusion with the increasing number of terminal ethyl groups introduced on the ligand, is understood to be due to the increase of intermolecular distance as suggested by the molecular volume, and also due to the increasing shielding effect by the terminal ethyl groups.

It is also noticed that ΔS_f decreases as ΔH_f decreases with an exception of $\text{Cu(Et}_2\text{acac)}_2$. Such parallel change of ΔS_f and ΔH_f can be often found in a series of hydrocarbon compounds. The change of entropy of fusion may be explained mainly in terms of the difference in crystal structure, if one remined that the structure of the chelate ring is found to be almost the same for all ligands and that the terminal ethyl groups are conceivably fixed in rather restricted spaces. Thus the difference of ΔS_f can be understood to be mainly due to the difference in ordering of the chelate molecules in the crystalline state.

As to the copper chelates of unsymmetric ligands, there is a possibility that the solid chelate is a mixture of *cis*- and *trans*-isomers, which may result in the lowering of melting point, lower than the expected value for one of the isomers. This effect must be most prominent for $\text{Cu(Et}_2\text{acac)}_2$, because the ligand is most unsymmetric. Thus, values of the thermodynamic parameters for $\text{Cu(Et}_2\text{acac)}_2$ do not fit in the general tendency of those of other chelates.

As discussed above, the melting point of bis(pentane-2,4-dionato)copper(II) lowers with the increasing number of ethyl groups introduced on 1- and/or 5-position. Although the result can be discussed semiquantitatively by the spectroscopic evidences as well as the thermodynamic data, the crystal structure data are needed for the more quantitative discussion of the melting point of these metal chelates.

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