# Crystal Structure of Bis-(1-*p*-*n*-octylphenylbutane-1, 3-dionato)-copper (II), A Complex Exhibiting Double Melting Behaviour

by

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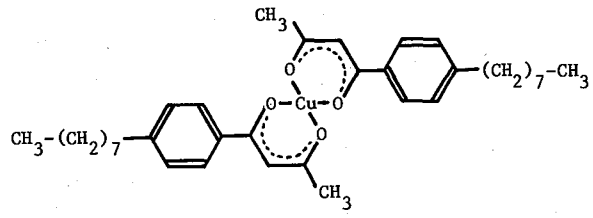
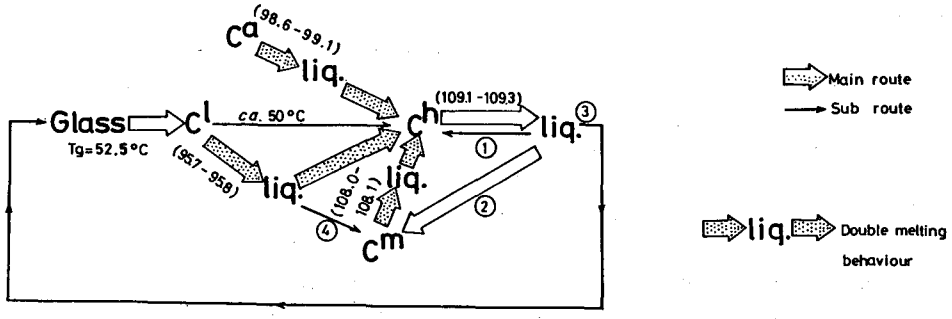
The complex, bis-(1-*p*-*n*-octylphenylbutane-1, 3-dionato)-copper (II), has four polymorphs with different m. p. s; $C^{l}$, $C^{a}$, $C^{m}$, and $C^{n}$. $C^{l}$, $C^{a}$, and $C^{m}$ exhibit double melting behaviour. The crystal structure of $C^{l}$ form of the complex has been determined by the single crystal X-ray analysis. Crystals are triclinic, space group $P\bar{1}$, with $a=24.18(1)$, $b=4.85(1)$, $c=8.78(1)$ Å, $\alpha=109.38(5)$, $\beta=115.19(5)$, $\gamma=97.32(5)°$. The structure was solved by the heavy atom method and refined to $R=0.118$ for 1656 reflections by the block-diagonal least-squares method. Since the complex has center of symmetry, the complex has *trans* form. The coordination to the copper atom is square planar. The octyl moiety takes a zigzag form. The packing of the molecules is close along *b* axis, but loose along *a* and *c* axes.

## 1. Introduction

During an attempt to synthesize a new mesomorphic compounds containing transition metal, the title complex (I) has been found to have four solid polymorphic forms; $C^1$, $C^a$, $C^m$, and $C^h$ (scheme) [1]. These forms have different melting points, and $C^1$, $C^a$, and $C^m$ exhibit the so-called double melting behaviour [1,2]. Related complexes having different *n*-alkyl chains have been prepared and the effect of the chain lengths on multiple melting behaviour have been discussed [2]. The structure and origin of the polymorphism of the title complex have been investigated by means of spectroscopic methods; all the four polymorphic forms have the square-planar *trans* coordination, and the polymorphism originates from the difference of the packing of *n*-octyl chains [3]. In order to confirm the spectroscopic interpretation as well as to reveal the packing of the complex in the crystal, $C^1$ form of the complex has been subjected to the single crystal X-ray analysis.




(I)




Scheme. The sequence of changes of state for bis-(1-*p*-*n*-octylphenylbutane-1,3-dionato)copper(II). Numbers in parentheses are m.p.s in °C [1].

## 2. Experimental

The synthesis of the complex was already described [4].

*Crystallographic measurement.* The crystals of the $C^1$ form are thin plates. A crystal cut to the size of 0.2x0.3x0.05 mm was used for X-ray measurement. Diffraction data were measured with Ni-filtered CuKα radiation on a microcomputer-controlled four-circle diffractometer [5]. The unit-cell dimensions were derived by a least-squares fit to the observed 2θ for 16 reflections. Crystal data are; $C_{36}H_{50}O_4Cu$, $M$=610.3, triclinic, space group $P\bar{1}$, $a$=24.18(1), $b$=4.85(1), $c$=8.78(1) Å, α=109.38(5), β=115.19(5), γ=97.32(5)°, $V$=833.8 Å$^3$, $Z$=1, $D_c$=1.215 g/cm$^3$. The diffraction profile was extremely broad and asymmetrical. Therefore ω-scan technique was used with the scan range of 2.8°+0.2°tanθ. Of 2248 independent reflections measured up to 2θ=120°, 1656 reflections whose intensities were greater than 2σ(I) were used for subsequent calculations. Two periodically monitored reflections showed no significant change in intensity during the data collection. The intensities were corrected only for the Lorentz and polarization factors.

*Structure determination.* The structure was solved by the heavy atom method, and refined by the block-diagonal least-squares method [6]. All hydrogen atoms except those of methyl groups were located in the difference Fourier synthesis calculated after the refinement with anisotropic temperature factors for the non-hydrogen atoms. The refinement including the hydrogen atoms reduced the $R$ value, $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, to 0.118 for 1656 reflections. The relatively high $R$ value might reflect poor quality of the intensity data due to the broad diffraction profile. The weighting scheme used at the final stage of the refinement was; $w$=1.0 for $F_o \leq 12$ and $w=[1.0+0.2(F_o-12)]^{-1}$ for $F_o > 12$. The final atomic parameters are given in Table 1. The list of observed and calculated structure factors, anisotropic temperature factors for the non-hydrogen atoms, and the atomic parameters for the hydrogen atoms are available from the authors on request. The atomic scattering factors were taken from the *International Tables for X-ray Crystallography* [7]. The computations were carried out on a HITAC M-150 computer at the Tottori University Computing Center.

## 3. Results and discussion

The bond lengths and angles for non-hydrogen atoms are shown in Table 2. Figure 1 shows the packing of the complex in this crystal form drawn by DCMS-3 [8].

Table 1. Final atomic parameters ($x10^4$) with estimated standard deviations in parentheses

| | $x$ | $y$ | $z$ | | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| Cu | 0(0) | 10000(0) | 5000(0) | C(9) | 2257(6) | 3603(34) | 5396(18) |
| O(1) | 177(3) | 9381(15) | 7211(9) | C(10) | 1871(6) | 4702(31) | 6015(17) |
| O(2) | 642(3) | 8368(17) | 4744(10) | C(11) | 2688(7) | 2403(38) | 3205(23) |
| C(1) | 558(5) | 8006(26) | 7828(14) | C(12) | 2759(6) | 3034(30) | 1765(18) |
| C(2) | 537(6) | 7458(8) | 9413(15) | C(13) | 3247(7) | 1763(34) | 1336(21) |
| C(3) | 941(5) | 6862(24) | 7159(14) | C(14) | 3334(7) | 2298(32) | -121(20) |
| C(4) | 988(5) | 7120(25) | 5704(14) | C(15) | 3823(7) | 1035(36) | -503(20) |
| C(5) | 1434(4) | 5951(24) | 5105(13) | C(16) | 3901(7) | 1397(34) | -2021(20) |
| C(6) | 1404(6) | 5964(31) | 3532(16) | C(17) | 4396(8) | 251(42) | -2339(23) |
| C(7) | 1810(6) | 4922(34) | 2910(18) | C(18) | 4487(9) | 679(50) | -3855(27) |
| C(8) | 2248(5) | 3742(28) | 3829(17) | | | | |

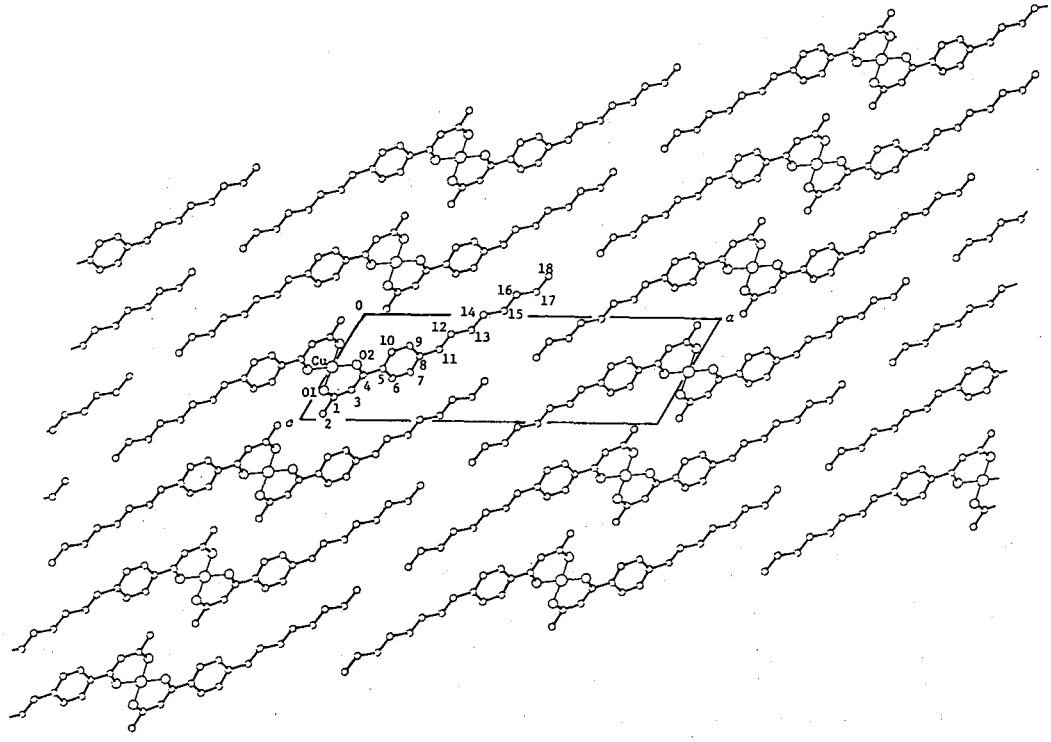



Fig. 1. Crystal structure of $C^1$ form of the complex viewed along the $b$ axis.

Table 2. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

| | | | | | |
|---|---|---|---|---|---|
| Cu-O(1) | 1.94(1) | Cu-O(2) | 1.89(1) | O(1)-C(1) | 1.25(2) |
| O(2)-C(4) | 1.28(2) | C(1)-C(2) | 1.52(2) | C(1)-C(3) | 1.37(2) |
| C(3)-C(4) | 1.37(2) | C(4)-C(5) | 1.48(2) | C(5)-C(6) | 1.35(2) |
| C(5)-C(10) | 1.37(2) | C(6)-C(7) | 1.38(2) | C(7)-C(8) | 1.35(2) |
| C(8)-C(9) | 1.39(2) | C(8)-C(11) | 1.51(3) | C(9)-C(10) | 1.35(2) |
| C(11)-C(12) | 1.47(3) | C(12)-C(13) | 1.53(2) | C(13)-C(14) | 1.48(3) |
| C(14)-C(15) | 1.51(3) | C(15)-C(16) | 1.49(3) | C(16)-C(17) | 1.47(3) |
| C(17)-C(18) | 1.51(3) | | | | |

| | | | |
|---|---|---|---|
| O(1)-Cu-O(2) | 92.9(4) | O(1)-Cu-O(2)$^{i}$ | 87.1(4) |
| Cu-O(1)-C(1) | 123.7(8) | Cu-O(2)-C(4) | 128.0(8) |
| O(1)-C(1)-C(2) | 112.7(11) | O(1)-C(1)-C(3) | 127.1(12) |
| C(2)-C(1)-C(3) | 120.1(11) | C(1)-C(3)-C(4) | 125.7(12) |
| O(2)-C(4)-C(3) | 122.2(12) | O(2)-C(4)-C(5) | 114.8(11) |
| C(3)-C(4)-C(5) | 123.0(11) | C(4)-C(5)-C(6) | 119.8(12) |
| C(4)-C(5)-C(10) | 123.8(12) | C(6)-C(5)-C(10) | 116.3(12) |
| C(5)-C(6)-C(7) | 122.4(14) | C(6)-C(7)-C(8) | 121.1(15) |
| C(7)-C(8)-C(9) | 116.3(15) | C(7)-C(8)-C(11) | 124.9(15) |
| C(9)-C(8)-C(11) | 118.7(15) | C(8)-C(9)-C(10) | 122.0(15) |
| C(5)-C(10)-C(9) | 121.8(14) | C(8)-C(11)-C(12) | 118.1(16) |
| C(11)-C(12)-C(13) | 113.8(14) | C(12)-C(13)-C(14) | 116.2(15) |
| C(13)-C(14)-C(15) | 114.9(15) | C(14)-C(15)-C(16) | 116.5(15) |
| C(15)-C(16)-C(17) | 116.1(16) | C(16)-C(17)-C(18) | 116.2(18) |

i) -x, 2-y, 1-z

The copper atom lies on the crystallographic center of symmetry. Thus the complex has center of symmetry. The geometry of the coordination is square-planar *trans*; the distances of Cu-O(1) and Cu-O(2) are 1.94(1) and 1.89(1) Å respectively, and the angles of O(1)-Cu-O(2) and O(1)-Cu-O(2)$^{i}$ are 92.9(4) and 87.1(4)° respectively. The O(1), O(2), and C(1)-C(5) atoms lie on a least-squares plane with root mean square deviation of 0.02 Å. This plane, as well as that through Cu and four oxygen atoms, and benzene ring are nearly coplanar. The octyl group takes zigzag form. These X-ray crystallographic results confirm the structure of this complex to be square-planar *trans* form which has been revealed by spectroscopic techniques [3].

In the $C^1$ form of this complex, the packing of the nearly planar molecule is parallel to each other. Close contacts between the molecules are observed along the *b*-axis; the interplanar distance is 3.34 Å. In contrast, there are little short contacts along the *a* or *c* axis. Thus the packing of the molecules is represented as columns along *b* direction being held loosely along *a* and *c* axes. Such packing might reflect the quite broad diffraction profiles and even streaked profiles occurred when the crystal was cut by razor blade; slippage between the columns might occur by small mechanical force. The crank-like molecule of this complex exhibits the double behaviour contrary to expectation of the mesomorphism. The reason might be that the present complex is less straight than bis{[(octyl-4-phenyl)-1-ethylenedithiolato-1,2](2-)-S,S'}nickel exihibiting smetic C mesomorphism [9]. Ohta *et al.* indicated on the basis of spectroscopic evidences that the molecular structure of the complex is same in all four crystal forms [2]. Presumably another forms of this complex might have different arrangement between the columns of this type. The packing of the molecules in the other form of this complex might provide useful information concerning the double melting behaviour.

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