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### Multiple Melting Behaviour in Square-planar trans-Bis-(1-p-n-alkylphenylbutane-1, 3-dionato)-copper (II)—The Effect of Alkyl Chain Length

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# Multiple Melting Behaviour in Square-planar *trans*-Bis-(1-*p*-*n*-alkylphenylbutane-1,3-dionato)-copper(II)—The Effect of Alkyl Chain Length

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The title complexes having different *n*-alkyl groups from methyl to dodecyl have synthesized. All these complexes exhibit solid polymorphism. The number of polymorphs depends on the length of the alkyl chain: two for *n* (the number of carbon atoms) = 0 ~ 2, three for *n* = 3 ~ 5 and 12, and four for *n* = 6 ~ 11, respectively. Each polymorphic form except those with the highest m.p.s. exhibits multiple melting behaviour: double melting for *n* = 0 ~ 5, 8, and 12, and triple melting for *n* = 6 ~ 11 except 8. The m.p.s. of the complexes with alkyl groups of odd carbon atoms are higher than those with even atoms, while the respective ligand solids show the opposite even-odd effect in their m.p.s.

## I INTRODUCTION

In a previous paper<sup>1</sup> it has been reported that *trans*-bis-(1-*p*-*n*-octylphenylbutane-1,3-dionato)copper(II) exhibits the solid polymorphism and three kinds of double melting behaviour.

Recently, Mueller-Westerhoff *et al.* have reported that *p*-*n*-alkyl-substituted square-planar styryl-dithiolato Ni complexes and the Pt complexes show smectic and nematic, depending on the length of the *p*-*n*-alkyl chains, while the Pd complexes have no mesomorphic properties at all.<sup>2</sup> The molecular

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structures of those complexes are very similar to our complexes. The mesomorphism and the solid polymorphism of these type of complexes would make a new field in the transition metal complex chemistry.

In the present work, bis-(1-*p*-*n*-alkylphenylbutane-1,3-dionato)copper(II) having different *n*-alkyl chains have been synthesized. We wish to report the solid polymorphism and the multiple melting behaviour of these complexes.

## II EXPERIMENTAL

The synthetic scheme of the present complexes is shown in Figure 1. The detailed procedures were almost the same as described for the case of octyl substituent in the previous paper.<sup>1</sup> For each alkyl substituent the yield of the first step was *ca.* 100 %. The ligands, 1-*p*-*n*-alkylphenylbutane-1,3-dione, were synthesized by the method reported by Beyer *et al.*<sup>3</sup> Table I are listed the yield, m.p.s., and elemental analysis data for these ligands. These compounds were purified by distillation under reduced pressure. The copper(II) complexes for each alkyl substituent were obtained according to the literature.<sup>4</sup> The purification of these complexes was made by recrystallization from acetone or ethanol more than twice. The elemental analysis data, crystallization solvents, and the crystalline shapes obtained are summarized in Table II. In some cases, a mixture of two crystal forms was obtained by crystallization from the solvents at room temperature. In the present work, each pure polymorphic form was not taken out for all complexes except for the case of *n*-octyl substituted complex, which was reported in details in the previous paper.<sup>1</sup>

The observation of all phase transitions of the present complexes was carried out by using a polarizing microscope equipped with a heating plate

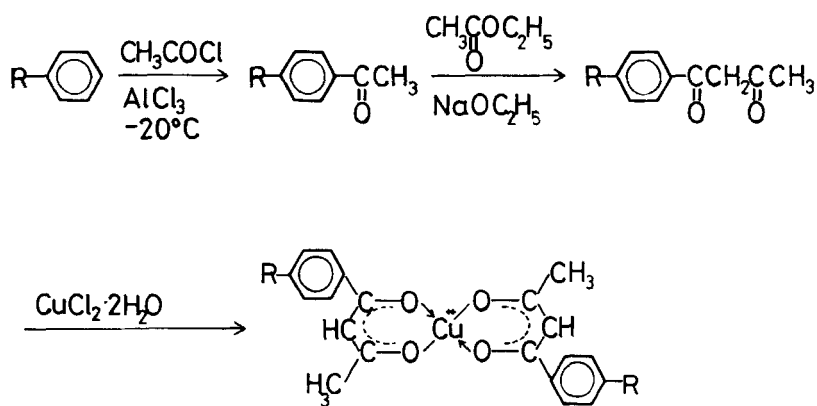


FIGURE 1 Synthetic scheme for bis-(1-*p*-*n*-alkylphenylbutane-1,3-dionato)copper(II).

TABLE I

Melting points, yield, and elemental analysis data for the ligands: 1-*p*-*n*-alkylphenylbutane-1,3-dione.

| Ligand                              | Yield (%) | Melting points (°C) | Elemental Analysis Found (Calcd) % |               |
|-------------------------------------|-----------|---------------------|------------------------------------|---------------|
|                                     |           |                     | H                                  | C             |
| R = H                               | Purchase  | 55–59               |                                    |               |
| R = CH <sub>3</sub>                 | 56        | 9.3                 | 6.76 (6.86)                        | 74.98 (74.96) |
| R = C <sub>2</sub> H <sub>5</sub>   | 83        | 0.7                 | 7.37 (7.42)                        | 75.11 (75.76) |
| R = C <sub>3</sub> H <sub>7</sub>   | 79        | 5.2                 | 7.83 (7.89)                        | 76.22 (76.44) |
| R = C <sub>4</sub> H <sub>9</sub>   | 78        | 27.2                | 8.12 (8.31)                        | 77.00 (77.03) |
| R = C <sub>5</sub> H <sub>11</sub>  | 87        | 33.0–34.0           | 8.59 (8.68)                        | 77.48 (77.55) |
| R = C <sub>6</sub> H <sub>13</sub>  | 77        | 35.5–37.1           | 9.02 (9.00)                        | 77.91 (78.01) |
| R = C <sub>7</sub> H <sub>15</sub>  | 83        | 27.0–29.5           | 9.35 (9.29)                        | 78.48 (78.42) |
| R = C <sub>8</sub> H <sub>17</sub>  | 81–87     | 39.0–41.0           | 9.69 (9.55)                        | 78.59 (78.79) |
| R = C <sub>9</sub> H <sub>19</sub>  | 74        | 25.5–27.0           | 9.85 (9.78)                        | 79.12 (79.12) |
| R = C <sub>10</sub> H <sub>21</sub> | 72        | 41.8–43.0           | 10.07 (10.00)                      | 79.11 (79.42) |
| R = C <sub>11</sub> H <sub>23</sub> | 87        | 39.0–40.0           | 10.31 (10.19)                      | 79.84 (79.70) |
| R = C <sub>12</sub> H <sub>25</sub> | 98        | 52.0–54.0           | 10.39 (10.37)                      | 79.80 (79.95) |

TABLE II

Elemental analysis data and recrystallization solvents for the complexes: square-planar *trans*-bis-(1-*p*-*n*-alkylphenylbutane-1,3-dionato)copper(II)

| Complexes                           | Elemental analysis Found (Calcd) % |               | Recrystallization solvents | Crystalline shapes obtained from recrystallization |
|-------------------------------------|------------------------------------|---------------|----------------------------|--|
|                                     | H                                  | C             |                            |  |
| R = H                               | 4.75 (4.70)                        | 62.06 (62.25) | Acetone                    | A mixture of striplike and needlelike              |
| R = CH <sub>3</sub>                 | 5.40 (5.36)                        | 63.82 (63.83) | Acetone                    | Rodlike  |
| R = C <sub>2</sub> H <sub>5</sub>   | 5.88 (5.93)                        | 64.95 (65.22) | Acetone                    | Plate  |
| R = C <sub>3</sub> H <sub>7</sub>   | 6.59 (6.43)                        | 66.29 (66.43) | Acetone                    | A mixture of microcrystal and Plate                |
| R = C <sub>4</sub> H <sub>9</sub>   | 6.88 (6.88)                        | 67.14 (67.51) | Acetone                    | A mixture of feathery and rodlike                  |
| R = C <sub>5</sub> H <sub>11</sub>  | 7.52 (7.28)                        | 68.33 (68.48) | Ethanol                    | Feathery   |
| R = C <sub>6</sub> H <sub>13</sub>  | 7.74 (7.64)                        | 69.10 (69.35) | Ethanol                    | A mixture of feathery and plate                    |
| R = C <sub>7</sub> H <sub>15</sub>  | 7.99 (7.96)                        | 69.96 (70.13) | Ethanol                    | A mixture of feathery and needlelike               |
| R = C <sub>8</sub> H <sub>17</sub>  | 8.27 (8.26)                        | 70.94 (70.85) | Acetone                    | Striplike  |
| R = C <sub>9</sub> H <sub>19</sub>  | 8.57 (8.53)                        | 71.45 (71.50) | Ethanol                    | A mixture of striplike and feathery                |
| R = C <sub>10</sub> H <sub>21</sub> | 8.83 (8.77)                        | 71.94 (72.09) | Ethanol                    | A mixture of feathery and striplike                |
| R = C <sub>11</sub> H <sub>23</sub> | 9.13 (9.00)                        | 72.57 (72.64) | Ethanol                    | A mixture of striplike, feathery, and needlelike   |
| R = C <sub>12</sub> H <sub>25</sub> | 9.32 (9.21)                        | 72.85 (73.14) | Acetone                    | A mixture of feathery and striplike                |

controlled by thermoregulator, Mettler FP5, within the accuracy of  $0.1^{\circ}\text{C}$ . A differential scanning calorimeter, Daini-Seikosha DSC SSC 560, was also used to establish the phase transitions.

### III RESULTS AND DISCUSSION

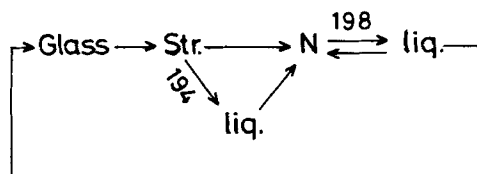
In Table III are given the m.p.s. of each polymorphic form along with the respective crystalline shape. When  $n$  (the number of carbon atoms in the  $n$ -alkyl substituent) = 0 ~ 2, each complex showed two polymorphic forms with different m.p.s., and when  $n$  = 3 ~ 5 and 12, three polymorphic forms were recognized. Furthermore, four kinds of polymorphic forms were recognized when  $n$  = 6 ~ 11. The observed number of m.p.s. of these complexes is strongly related to the length of the alkyl group. Although only a m.p. of  $190\text{--}190^{\circ}\text{C}$  had been reported in the core complex corresponding to the  $n$  = 0 case by Ribeiro da Silva *et al.*,<sup>5</sup> it was found in the present work that this complex has two m.p.s at  $194^{\circ}\text{C}$  and  $198^{\circ}\text{C}$ , which could be confirmed by the microscope observation and the DSC measurement.

In the previous paper, we described that the solid polymorphism is originated not from the change of co-ordination of ligands, *i.e.*, *cis-trans* isomerization, but mainly from the different packing of  $n$ -alkyl chains. However, the presently observed solid polymorphism in the core complex and the complexes having relatively short alkyl chains indicates that another origin might be operative in these complexes. Although the origin is not clear at the present stage, it should be noted here that a possibility of the *cis-trans* isomerization change would be excluded, because two polymorphic forms isolated in the case of the ethyl substituent gave the same far-infrared spectra. This indicates that the *cis-trans* isomerization would not occur. The large difference was observed in the region from  $750$  to  $850\text{ cm}^{-1}$  of their infrared spectra.

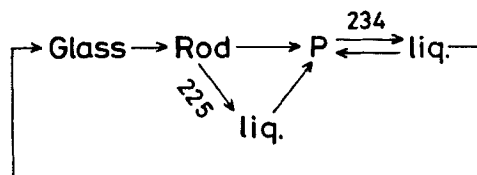
Figure 2 shows the sequence of the state changes for each complex from  $n$  = 0 to 12, which was confirmed mainly by the microscopic observation. The complexes having the relatively long alkyl tails showed much more complicated state changes. When  $n$  = 6 ~ 11 except  $n$  = 8, all complexes exhibited so-called triple melting behaviour, and other complexes also exhibited double melting behaviour. In the nonyl substituted complex, for example, when the strip-like (long thin) polymorphic form was heated from room temperature, it melted at  $102^{\circ}\text{C}$  except for a portion transformed by a solid-solid phase transition from the strip-like to the needle-like, and then the melt resolidified completely into the needle-like crystal; on further heating, it melted at  $120^{\circ}\text{C}$  except for a portion transformed by a next slow solid-solid phase transition from the needle-like to the plate-like crystal,

TABLE III  
Melting points and crystalline shapes of the polymorphs for *p*-*n*-alkyl derivatives of bis(1-phenylbutane-1,3-dionato)copper(II).

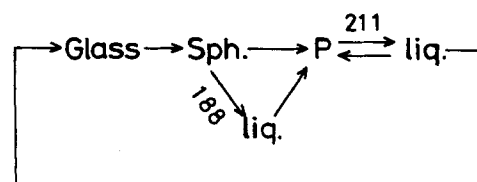
| Complexes                        | Melting points (°C)  | Crystalline shapes                        | Complexes                         | Melting points (°C)  | Crystalline shapes    |
|----------------------------------|--|---|-----------------------------------|--|-----------------------|
| R=H                              | Tm <sub>1</sub> = 194.2–194.5<br>Tm <sub>2</sub> = 197.9–198.2   | striplike<br>needle                       | R=C <sub>8</sub> H <sub>17</sub>  | Tm <sub>1</sub> = 95.7–95.8<br>Tm <sub>2</sub> = 98.6–99.1     | striplike<br>feathery |
| R=CH <sub>3</sub>                | Tm <sub>1</sub> = 224.5–226.2<br>Tm <sub>2</sub> = 233.7–233.9   | rodlike<br>plate                          |                                   | Tm <sub>3</sub> = 108.0–108.1<br>Tm <sub>4</sub> = 109.1–109.3 | spherulite<br>rodlike |
| R=C <sub>2</sub> H <sub>5</sub>  | Tm <sub>1</sub> = 188.0–188.5<br>Tm <sub>2</sub> = 210.8–211.3   | spherulite<br>plate                       | R=C <sub>9</sub> H <sub>19</sub>  | Tm <sub>1</sub> = 102.0–102.5<br>Tm <sub>2</sub> = 115.3–116.3 | striplike<br>feathery |
| R=C <sub>3</sub> H <sub>7</sub>  | Tm <sub>1</sub> = 168.6–168.8<br>Tm <sub>2</sub> = 169.8–170.0<br>Tm <sub>3</sub> = 171.5–171.9                                  | microcrystal<br>spherulite<br>plate       |                                   | Tm <sub>3</sub> = 120.0–120.4<br>Tm <sub>4</sub> = 120.8–120.9 | needle<br>plate       |
| R=C <sub>4</sub> H <sub>9</sub>  | Tm <sub>1</sub> = 142.0–143.0<br>Tm <sub>2</sub> = 152.3–152.5<br>Tm <sub>3</sub> = 154.3–154.6                                  | feathery<br>spherulite<br>rodlike         | R=C <sub>10</sub> H <sub>21</sub> | Tm <sub>1</sub> = 100.2–100.7<br>Tm <sub>2</sub> = 102.3–102.5 | feathery<br>striplike |
|                                  |  |   |                                   | Tm <sub>3</sub> = 102.7–102.8<br>Tm <sub>4</sub> = 107.0–107.4 | plate<br>needle       |
| R=C <sub>5</sub> H <sub>11</sub> | Tm <sub>1</sub> = 140.4–140.8<br>Tm <sub>2</sub> = 146.1–146.4<br>Tm <sub>3</sub> = 147.5–147.7                                  | feathery<br>spherulite<br>plate           | R=C <sub>11</sub> H <sub>23</sub> | Tm <sub>1</sub> = 107.0–107.4<br>Tm <sub>2</sub> = 113.8–114.2 | striplike<br>feathery |
|                                  |  |   |                                   | Tm <sub>3</sub> = 117.6–117.8<br>Tm <sub>4</sub> = 118.6–118.8 | needle<br>plate       |
| R=C <sub>6</sub> H <sub>13</sub> | Tm <sub>1</sub> = 118.8–119.2<br>Tm <sub>2</sub> = 120.2–120.7<br>Tm <sub>3</sub> = 125.3–125.5<br>Tm <sub>4</sub> = 126.3–126.5 | feathery<br>plate<br>spherulite<br>needle | R=C <sub>12</sub> H <sub>25</sub> | Tm <sub>1</sub> = 104.9–105.5<br>Tm <sub>2</sub> = 107.0–107.2 | feathery<br>striplike |
|                                  |  |   |                                   | Tm <sub>3</sub> = 107.8–108.0                                  | plate                 |
| R=C <sub>7</sub> H <sub>15</sub> | Tm <sub>1</sub> = 125.2–125.5<br>Tm <sub>2</sub> = 128.3–128.5<br>Tm <sub>3</sub> = 129.2–129.5<br>Tm <sub>4</sub> = 130.0–130.2 | feathery<br>needle<br>spherulite<br>plate |                                   |  |                       |

$n = 0$ 

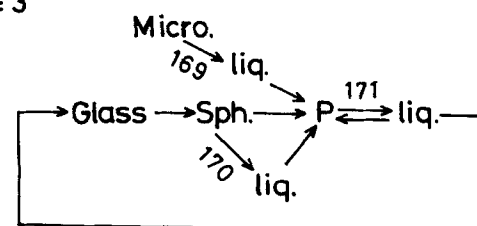
Double melting

 $n = 1$ 

Double melting

 $n = 2$ 

Double melting

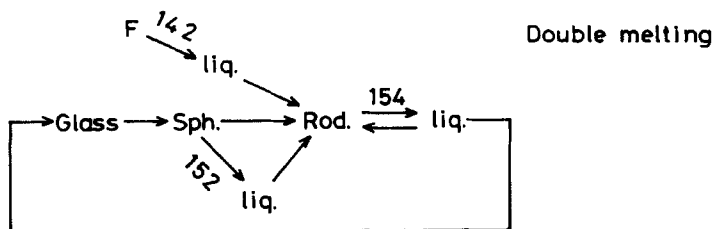
 $n = 3$ 

Double melting

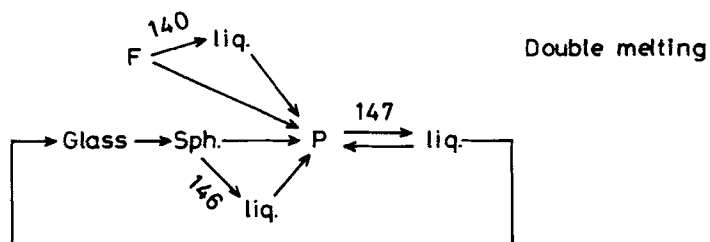
FIGURE 2 The sequences of changes of state for bis-(1-*p*-*n*-alkylphenylbutane-1,3-dionato) copper(II). “*n*” is the number of carbon atoms in the *n*-alkyl group. Numbers in the figure are m.p.s. Nomenclature of crystalline shape is: Str. = striplike (long thin), N = needle-like, Rod = rodlike, P = plate, Sph. = spherulite, F = feathery (hair-like), and Micro. = micro-crystal.



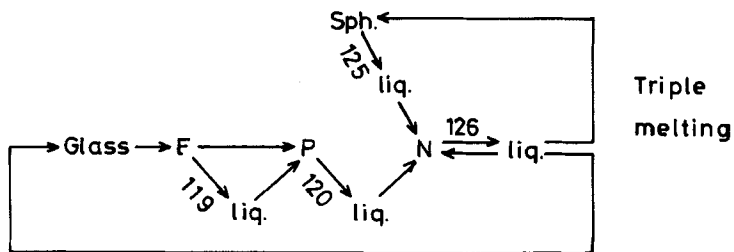
$n=4$



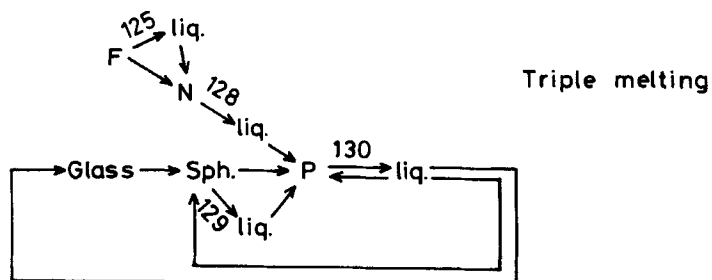
$n=5$



$n=6$

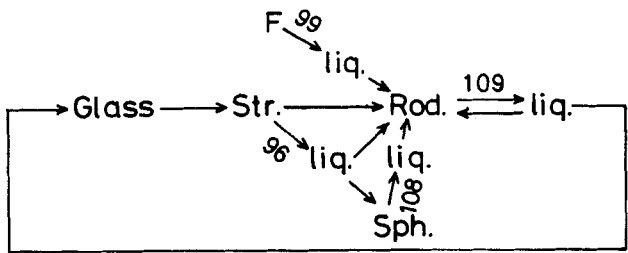


$n=7$



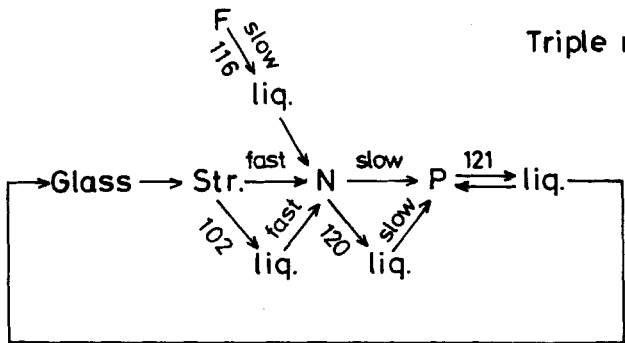
n = 8

Double melting



n = 9

Triple melting



n = 10

Triple melting

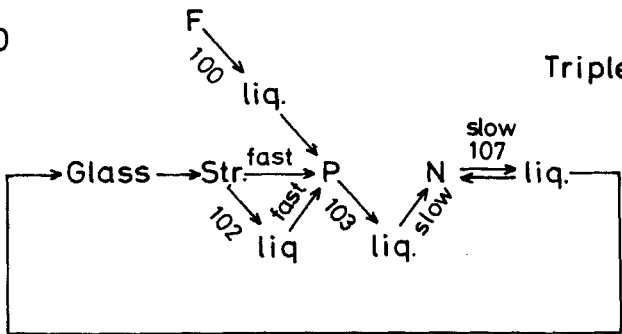
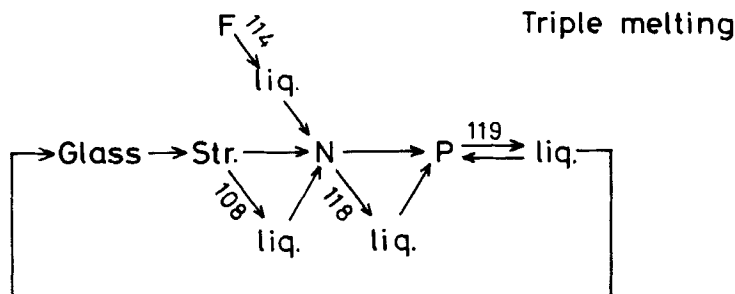
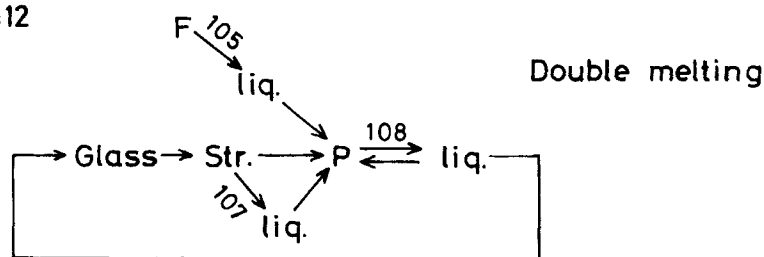


FIGURE 2 (cont.)

$n=11$



$n=12$



and then the melt resolidified into the plate-like crystals of the most stable polymorphic form; on further heating, it melted completely at 121°C. Thus, the triple melting behaviour was observed on one heating stage.

As shown in Figure 3, the even-odd effect in the melting points of the complexes was found when  $n = 6 \sim 12$ . Namely, the m.p.s of the complexes having odd number of carbon atoms in the  $n$ -alkyl group are higher than those of the even numbered complexes. On the contrary, the even-odd effect in the m.p.s of the respective ligands is quite opposite, as shown in Figure 4. To our knowledge, such a phenomenon seems to be the first example in the transition metal complexes.

Malikin<sup>6</sup> suggested about long-chain compounds that the crystalline structure of odd members would be expected to be less stable, which is in agreement with their lower m.p.s. However, higher alkyl iodides with an odd carbon content melt at the higher temperature. He inferred in his paper that this was probably due to the large iodine atom having the same effect as an additional carbon atom, and thus giving an even chain the properties of an odd. Although his inference seems to be useful, this could not be appreciated with ease to our complexes because of the great difference of these molecular structures. Further investigation is required for this problem.

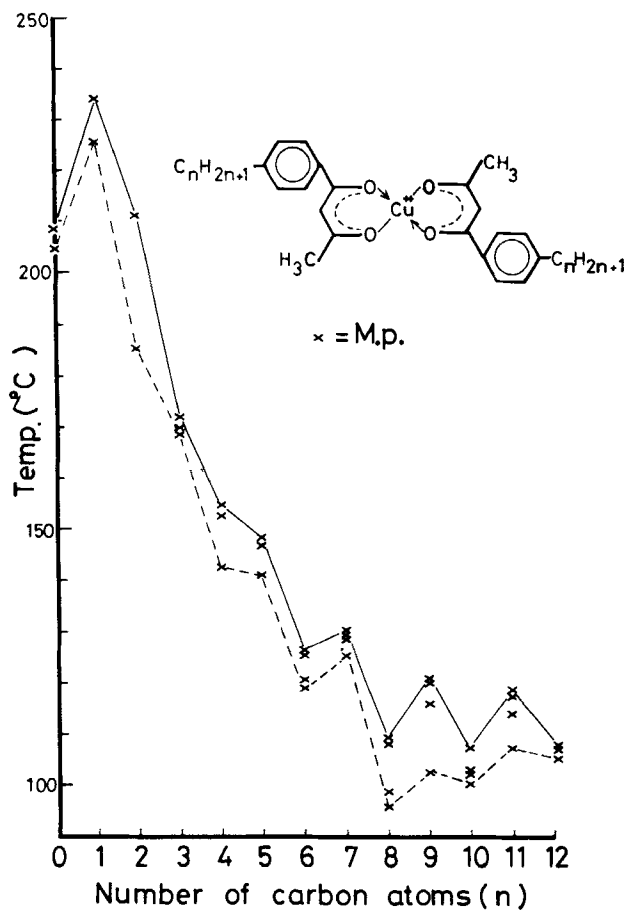


FIGURE 3 Melting points versus chain length for the series of bis-(1-*p*-*n*-alkylphenylbutane-1,3-dionato)copper(II). See Table III.

#### IV SUMMARY

Square-planar *trans*-bis-(1-*p*-*n*-alkylphenylbutane-1,3-dionato)copper(II) complexes exhibit the multiple melting behaviour and the opposite even-odd effect in their m.p.s. between the ligands and the corresponding complexes.

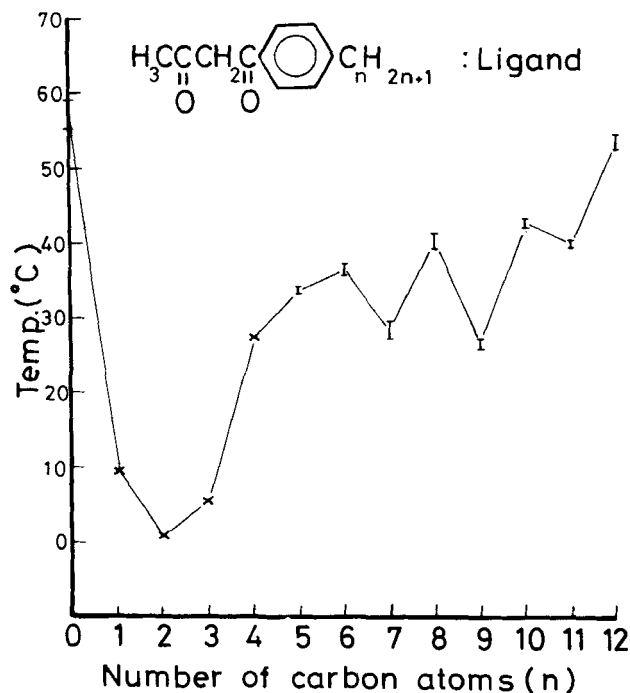


FIGURE 4 Melting points versus chain length for the series of 1-p-n-alkylphenylbutane-1,3-dione (ligands). See Table I.

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