

Square-planar *trans*-Bis-(1-*p*-n-octylphenylbutane-1,3-dionato)copper(II), a New Compound exhibiting Three Kinds of 'Double Melting' Behaviour

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Summary The new compound, square-planar *trans*-bis-(1-*p*-n-octylphenylbutane-1,3-dionato)copper(II) has four polymorphs, C^l (m.p. 96 °C), C^a (99 °C), C^m (108 °C), and C^h (109 °C); C^l, C^a, and C^m exhibit double-melting behaviour.

THE title complex was investigated in an attempt to synthesise a new mesomorphic compound containing a transition metal. This complex does not have a mesomorphic state, but exists in four solid polymorphic forms: C^l, C^a, C^m, and C^h with different melting points (Figure). Interestingly, C^l, C^a, and C^m exhibit the so-called double melting behaviour,¹ C^l only on very rapid heating, and C^a and C^m only on very slow heating. So far as we know, this is the first compound of the ML₂ type (M = transition metal, L = ligand) with a long alkyl chain which has three double melting forms.

All m.p.'s and phase transitions are shown in the Figure. Each polymorph could be obtained as a stable solid at room temperature and was identified mainly by X-ray powder diffraction.

TABLE. X-Ray diffraction data with relative intensities (I/I_1) for the four strongest lines in each polymorph.

C ^h	$d\text{\AA}$	11.05	4.00	8.04	3.74
	I/I_1	100	89	43	38
C ^m	$d\text{\AA}$	10.28	8.51	4.25	9.72
	I/I_1	100	51	37	34
C ^a	$d\text{\AA}$	10.51	4.13	8.27	6.86
	I/I_1	100	98	91	61
C ^l	$d\text{\AA}$	4.10	6.97	5.99	3.66
	I/I_1	100	100	68	51

When C^l was rapidly heated (>10 °C/min), a solid mixture of C^l and C^h was obtained because of a relatively slow solid-solid phase transition from C^l to C^h at *ca.* 50 °C. The

C^l crystals in the mixture melted at the m.p. of C^l, 95.7–95.8 °C, and then the melt resolidified completely in the C^h form because of the presence of seed crystals of C^h formed by the solid-solid phase transition; on further heating, the C^h crystals melted finally at the m.p. of C^h, 109.1–109.3 °C. However, when C^l was heated very slowly (<2.5 °C/min) from room temperature, the complete solid-solid phase transition occurred below the m.p. of C^l, and therefore only a single m.p. of C^h was observed. When C^l crystals at room temperature were brought into contact with a bath at 106.0 °C, a mixture of crystals of C^h and C^m was obtained (route 4 in the Figure).

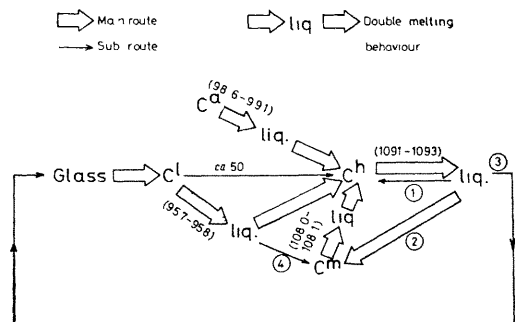


FIGURE The sequence of changes of state for square-planar *trans*-bis-(1-*p*-n-octylphenylbutane-1,3-dionato)copper(II): (1) very slow cooling; (2) slow cooling; (3) rapid cooling; (4) see main text. Numbers in parentheses are m.p.s. in °C.

When C^m was heated very slowly (<0.1 °C/min) from room temperature, a solid-solid phase transition was not observed and it melted completely at its m.p. of 108.0–108.1 °C; the melt then resolidified in the C^h form and on further heating it melted again at the m.p. of C^h, 109.1–109.3 °C. However, when C^m was rapidly heated (>1.0 °C/min) from room temperature up to 110 °C, only a single m.p., that of C^m, was observed.

C^a exhibited double-melting behaviour without a solid-solid phase transition. At a heating rate of <10 °C/min, C^a melted at its m.p., 98.6–99.1 °C, and then resolidified as C^h. C^h has, of course, only a single m.p.

The square-planar *trans*-bis(1-*p*-n-octylphenylbutane-1,3-dionato)copper(II) and its polymorphs: C^l, C^a, C^m, and C^h were prepared as follows. From *p*-n-octylacetophenone synthesised by the method of Giroud *et al.*,² 1-*p*-n-octylphenylbutane-1,3-dione was obtained following the method of Beyer *et al.*³ and its copper(II) complex was prepared by the method of Hon *et al.*⁴ This gave satisfactory C and H analyses, and showed λ_{\max} (n-hexane) 264 (ϵ 39,000), 293 (26,000), 324 (51,000), 549 (40.1), and 662 (48.0) nm. Its electronic, far-i.r., and Raman spectra, to be reported elsewhere, provided evidence for its *trans*-square-planar structure, as for bis-(1-phenylbutane-1,3-dionato)copper(II).⁴ No changes in co-ordination mode were observed in the four polymorphic forms.

C^l was obtained as green striplike crystals by recrystallization at 5 °C from boiling methanol, ethanol, acetone, or n-hexane. C^a was obtained as green crystals by evaporation of an acetonitrile solution at 30–32 °C during about 1 month. C^m, which could not be obtained by recrystallization, could be obtained as green lustrous spherulites by slow cooling of the melt from about 140 °C. C^h, grey-green microcrystals, was prepared by solution phase transformation,⁵ *i.e.*, C^l was added to acetonitrile in excess of its solubility limit and the solution temperature was kept at 50 °C for about 20 min. With this procedure C^l was transformed completely into C^h. A glass, which is stable at room temperature, was obtained when the melt was dipped into liquid nitrogen.

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¹ The multiple melting behaviour of glycerides is well known: D. Chapman, *Chem. Rev.*, 1962, **62**, 433

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