Mesogenic Properties of Copper(II) Complexes formed from α-Substituted β-Dialdehydes and β-Diketones

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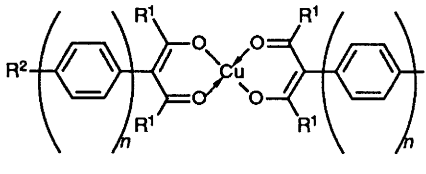
The relationship between molecular structure and mesogenic properties is explored for copper(II) complexes of α-substituted β-dialdehydes and β-diketones. The copper(II) complex of *p*-pentylphenylmalonaldehyde shows a nematic phase, but the presence of off-axial substituents or the removal of the aromatic ring precludes mesophase formation.

In recent years a number of metal complexes have been reported which show liquid-crystal phases for example refs. 1–6. Understanding of the relationship between molecular structure and mesophase behaviour of such compounds is still at an elementary stage. In the case of β-diketone complexes, compounds of type **1** with R^1 a long, linear group (*e.g.* alkoxybiphenyl), R^2 = H and $n = 0$, have been found to show discotic behaviour.[1] Compounds of type **1** with R^1 a small group and R^2 a long one might be expected, by analogy with organic liquid crystals derived from biphenyl and *p*-terphenyl, to form nematic or smectic phases. If the two six-membered chelate rings function like two benzene rings, complexes with $n = 0$ might show similar properties to 4,4′-disubstituted biphenyls; if the chelate system more closely mimics a single benzene ring, as suggested by Giroud and Meuller-Westerhoff[7] for bis(dithiolato) complexes of nickel, those with $n = 1$ might resemble the analogous terphenyls in their behaviour. We have accordingly prepared compounds with $n = 0$ or 1 and examined their mesogenic properties.

In organic systems the introduction of off-axial groups does not necessarily destroy mesogenic properties, and it has also recently been shown that complexes **2**, with an off-axial bridge, have smectic phases extending in some cases over a range of 110 °C.[2] Accordingly, we have examined the effect of the presence or absence of off-axial methyl groups (R^1 = Me or H) in molecules of type **1**.



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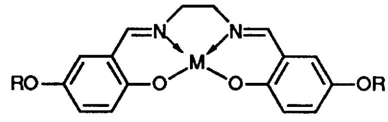

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M = Cu or Ni; R = C_nH_{2n+1} (n = 4 – 8)

Results and Discussion

The results are summarized in Table 1. Complexes **1a**–**1c** are derived from substituted malonaldehydes, and **1d**–**1f** from acetylacetones (pentane-2,4-diones). As expected, no liquid crystalline phases are formed when R^2 is small (compound **1b** and **1e**). When R^2 is pentyl, mesogenic behaviour is found for $n = 1$ and R^1 = H (compound **1c**), but not for $n = 0$ or R^1 = Me (compound **1a**, **1d** and **1f**). This implies that the chelate system behaves more like a single benzene ring than two, and needs to be kept slim for liquid crystals to be obtained, in contrast to the behaviour for complexes **2**. The mesophase formed by **1c** is nematic and extends over about 10 °C before decomposition at *ca.* 230 °C. In contrast, the analogous organic di-pentyl derivatives of *para* bi-, ter- and quater-phenyl show only smectic mesophases (biphenyl, 12–52; terphenyl, 192–213; quaterphenyl, 297–352 °C).[8] The rough similarity of the mesophase temperature range of **1c** with that of the analogous terphenyl further supports the idea that two chelate rings in a complex have roughly the same effect as a single benzene ring. We studied the pentyl derivative because of the ready availability of starting materials for these; longer alkyl chains might be expected to enhance mesogenic behaviour somewhat. Room-temperature magnetic moments and visible spectra are as expected for these complexes, but preliminary low-temperature magnetic studies of **1a**–**1f** suggest that further investigation of the mesogenic complex **1c** will be profitable. The magnetic moments of complexes **1c**–**1f** are on the high side of the range expected for copper(II) complexes of this type, but this may not be significant. We did not study the corresponding nickel(II) complexes because preliminary investigations suggested that these were polymeric species with octahedral co-ordination of the nickel. This is in line with the finding of Fackler and Cotton[9] that the nickel analogue of complex **1e** polymerises irreversibly in the solid state.

Experimental

Preparation of Dialdehydes and Diketones.—Phenylmalonaldehyde was prepared by the method of Coppola *et al.*[10] and purified by sublimation (m.p. 89–93 °C; lit.,[10] 92–95 °C). 3-Pentylpentane-2,4-dione was purchased from Aldrich. 3-Phenylpentane-2,4-dione was made by the method of Hauser and Manyik[11] (m.p. 55–57 °C; lit.,[11] 58.5–59.5 °C). The remaining compounds were synthesized as follows.

Pentylmalonaldehyde. The *sodium salt* was prepared from heptanal by (*i*) formation of the diethyl acetal using triethyl orthoformate;[12] (*ii*) conversion to 2-pentyl-3-ethoxyprop-2-enal by the method of Nair *et al.*[13] and (*iii*) hydrolysis with

Table 1 Phase properties of complexes **1**

Complex	*n*	R^1	R^2	Phases (Transition temperature/°C)
1a	0	H	C_5H_{11}	Crystalline (144)/isotropic liquid
1b	1	H	H	Crystalline (233^a)/isotropic liquid
1c	1	H	C_5H_{11}	Crystalline (220)/nematic liquid (230^a)/isotropic liquid
1d	0	Me	C_5H_{11}	Crystalline (180)/isotropic liquid
1e	1	Me	H	Crystalline (235^b)/isotropic liquid
1f	1	Me	C_5H_{11}	Crystalline (171)/isotropic liquid

[a] With decomposition. [b] Lit.,[16] 222–224 °C.

aqueous sodium hydroxide. Evaporation of the resulting solution gave a white powder (Found: C, 46.3; H, 8.35. $C_8H_{13}NaO_2{\cdot}2.4H_2O$ requires C, 46.3; H, 8.65%); δ_H-(D_2O;$SiMe_4$) 0.85, 1.3, 2.1 (3 H, 6 H, 2 H; C_5H_{11}), 3.2 (0.35 H, ?) and 8.35 (2 H, 2 CH). The salt was recrystallized from ethanol–diethyl ether before use.

p-*Pentylphenylmalonaldehyde*. This was prepared from pentylbenzene by (*i*) Friedel–Crafts acetylation; (*ii*) conversion of $-COCH_3$ to $-CH_2CO_2H$ by the Willgerodt–Kindler reaction[14] and (*iii*) conversion of $-CH_2CO_2H$ to $-CH(CHO)_2$ according to Coppola *et al.*[10] Recrystallization from light petroleum (b.p. 60–80 °C) gave pale yellow *crystals*, m.p. 84–86 °C (Found: C, 76.9; H, 8.3. $C_{14}H_{18}O_2$ requires C, 77.0; H, 8.30%); δ_H($CDCl_3$; $SiMe_4$) 0.9, 1.35, 1.6, 2.6 (3 H, 4 H, 2 H, 2 H; C_5H_{11}), 7.2 (4 H, C_6H_4), 8.6 (2 H, 2 CH) and 14.3 (1 H, OH of enol form).

3-(p-*Pentylphenyl*)*pentane*-2,4-*dione*. This was prepared from pentylbenzene by (*i*) conversion into *p*-pentylphenylacetic acid as above; (*ii*) formation of the acid chloride with thionyl chloride; (*iii*) conversion of $-CH_2COCl$ to $-CH_2COCH_3$ according to Walker and Hauser[15] and (*iv*) acetylation of $-CH_2COCH_3$ by the method of Hauser and Manyik.[11] Redistillation gave a pale yellow liquid, b.p. 125 °C (0.1 mm Hg, ≈ 13.3 Pa) (Found: C, 77.8; H, 8.95. $C_{16}H_{22}O_2$ requires C, 78.0; H, 9.00%); δ_H($CDCl_3$; $SiMe_4$) 0.9, 1.35, 1.65, 2.6 (3 H, 4 H, 2 H, 2 H; C_5H_{11}), 1.9 (6 H, 2 CH_3), 7.1 (4 H, C_6H_4) and 16.7 (1 H, OH of enol form).

Preparation of Complexes.—The complexes were prepared by mixing solutions of the dialdehyde or diketone and copper(II) acetate in water, aqueous methanol or methanol and recrystallizing the precipitate. For pentylmalonaldehyde an aqueous solution of the sodium salt was used, neutralized to pH 7 with hydrochloric acid. The products obtained were as follows.

1a. Bluish green *crystals* [from light petroleum (b.p. 60–80 °C)], μ_{eff} 1.85, visible spectrum ($CHCl_3$) 15 650 and 19 450 cm^{-1} (Found: C, 56.0; H, 7.65. $C_{16}H_{26}CuO_4$ requires C, 55.6; H, 7.60%).

1b. Yellowish green *crystals*, μ_{eff} 1.87, visible spectrum ($CHCl_3$) 15 600 cm^{-1} * (Found: C, 59.7; H, 3.95. $C_{18}H_{14}CuO_4$ requires C, 60.4; H, 3.95%).

1c. Fine yellowish green *needles* (from ethanol), μ_{eff} 1.93, visible spectrum (CCl_4) 15 450 cm^{-1} * (Found: C, 67.0; H, 6.85. $C_{28}H_{34}CuO_4$ requires C, 67.5; H, 6.90%).

1d. Fine light-grey *needles* (from ethanol), μ_{eff} 1.91, visible spectrum (CCl_4) 15 650 and 20 100 cm^{-1} (Found: C, 59.2; H, 8.4. $C_{20}H_{34}CuO_4$ requires C, 59.8; H, 8.50%).

1e. Brownish green *crystals*[16] [from chloroform–light petroleum (b.p. 60–80 °C)], μ_{eff} 1.94, visible spectrum (CCl_4) 15 650 and 19 550 cm^{-1} (Found: C, 63.7; H, 5.4. Calc. for $C_{22}H_{22}CuO_4$: C, 63.8; H, 5.35%).

1f. Brownish green *crystals* (from aqueous ethanol), μ_{eff} 1.90, visible spectrum (CCl_4) 15 500 and 19 600 cm^{-1} (Found: C, 69.4; H, 7.65. $C_{32}H_{42}CuO_4$ requires C, 69.3; H, 7.65%).

When 3-(*p*-pentylphenyl)pentane-2,4-dione was treated with nickel(II) acetate in aqueous ethanol, a green precipitate was obtained which could not be recrystallized. The green colour is in accord with a $Ni^{II}O_6$ species.

Phase Studies.—The phase behaviour of the complexes was examined by means of a Mettler FP5 hot stage and controller in conjunction with an Olympus BH2 polarizing microscope. Both heating to, and cooling from, the isotropic liquid were studied for each complex and the results are given in Table 1.

Magnetic Susceptibilities.—Room-temperature magnetic susceptibilities were obtained on solid samples using a SHE SQUID magnetometer. Calibration and operation of the SQUID are described elsewhere.[17,18] The magnetic moment of complex **1c** was also measured in chloroform solution by the Evans' NMR method[19,20] as $\mu_{eff} = 1.89$.

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* The second d–d band is obscured by a strong UV-absorption tail.