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Crystal and Molecular Structure of the Discogen bis[1,3-di(p-n-octylphenyl)propane-1,3-dionato]copper(II)†

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The transition metal containing discogen bis[1,3-di(p-n-octylphenyl)propane-1,3-dionato]copper(II) crystallizes in the triclinic space group P$\bar{1}$. The copper atom lies on an inversion centre and is surrounded by four oxygen atoms in a square planar arrangement. The octyl chains are fully extended in an all-trans conformation. The molecules form a tilted columnar arrangement, the angle of tilt between the disc normal and the column axis being 122°. The column axis coincides with the crystallographic *a*-axis. In the crystal structure, each column is surrounded by six others. Along the column axis, adjacent copper atoms are separated by 5.821(3)Å.

Keywords: Discotic, copper complex, crystal structure

INTRODUCTION

We have earlier reported the crystal structure analyses of the discogenic transition metal complexes bis[1,3-di(p-n-octyloxyphenyl) propane-1,3-dionato]copper(II)[1] and bis[1,3-di(p-n-decylphenyl)propane-1,3-dionato]palladium(II),[2] referred to as Cu—OC_8H_{17} and Pd—$C_{10}H_{21}$ respectively. In this paper, we present the details of the investigations on bis[1,3-di(p-n-octylphenyl)propane-1,3-dionato]copper(II), referred to as Cu—C_8H_{17} hereafter, using single crystal X-ray diffraction.

EXPERIMENTAL

The synthesis of Cu—C_8H_{17} has been reported earlier by Ohta *et al.*[3] In the present study, the synthesis was carried out according to the scheme shown in Figure 1.

† Presented at the 13th International Liquid Crystal Conference, Vancouver, Canada, 22–27 July 1990.

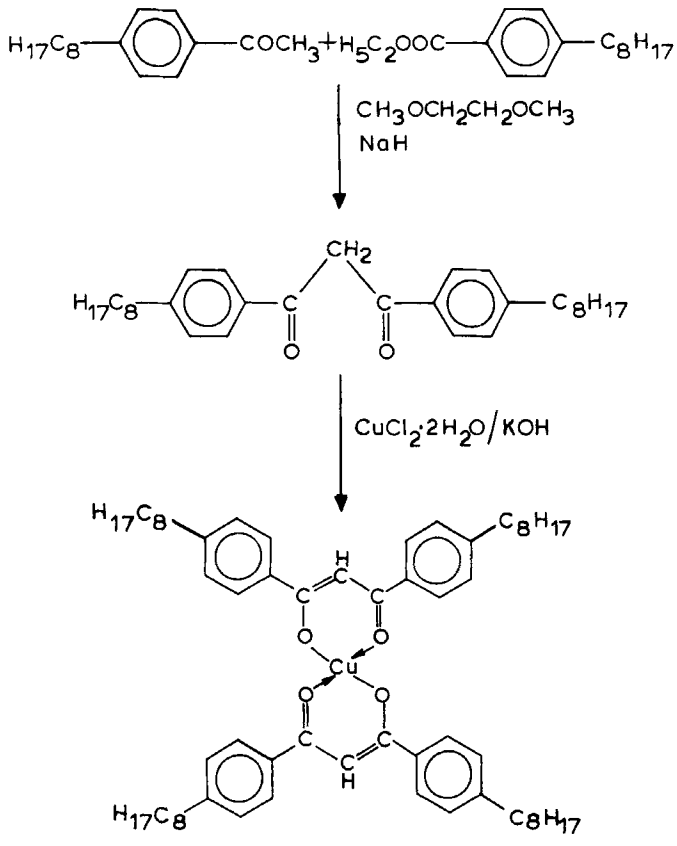

FIGURE 1 Synthetic route for the preparation of Cu—C_8H_{17}.

The detailed experimental procedure is similar to that described by us previously.[4] The complex was crystallized several times from acetone. The transition temperatures obtained are as follows:

$$K \xrightarrow{76.0} M \underset{}{\overset{141.5°C}{\rightleftharpoons}} I$$

Transparent, green coloured, needle-like crystals of Cu—C_8H_{17} were grown by slow evaporation from a solution in acetone. The unit cell dimensions were determined and refined by least squares procedure, using 18 reflections on a CAD-4 single crystal diffractometer. Table I lists the crystal data and other relevant details of the structure analysis.

It must be mentioned that using acetone as the solvent, in addition to the needle-like crystals, some prismatic crystals were also found to crystallize. However, the prismatic form was found to be less abundant. Characterization of the prismatic crystals by X-rays indicated that their unit cell data are different from those of the needle-like crystals. Further details concerning the prismatic form will be reported at a later stage.

TABLE I

Crystal data and relevant details of the analysis

Molecular formula	$C_{62}H_{86}O_4Cu$
a	5.821(3)Å
b	14.332(1)
c	17.630(2)
α	107.35(1)°
β	98.86(2)
γ	93.58(3)
V	1378 Å^3
Z	1
Space group	$P\bar{1}$
ρ calc	1.148 gm/cc
μ MoK_α	4.57 cm^{-1}
λ MoK_α	0.7107 Å
Data collection	CAD4 diffractometer
Scan mode	ω/2θ
Scan speed	5.5°/min
Independent reflections	4890
Reflections with $I \geq 3\sigma(I)$	1980
Corrections applied	Lp, absorption,[8] anomalous scattering[9] for Cu
Scattering factors	Cu (Ref. 9) C, O (Ref. 10) H (Ref. 11)
R	0.055
R_w	0.054
Weighting scheme	$K/[\sigma^2(F) + g(F)^2]$ K = 2.3062, g = 0.000109

STRUCTURE DETERMINATION

The statistical distribution of the normalized structure factors[5] indicated the space group to be centric, $P\bar{1}$ and with $Z = 1$, the copper atom has to lie on an inversion centre. Placing the copper atom at (0,0,0), a difference electron density map was computed from which the positions of the rest of the non-hydrogen atoms in the molecule were identified. Using the program package SHELX-76,[6] the positional and the anisotropic thermal parameters of all the non-hydrogen atoms were refined by full-matrix least squares procedure. Although all the hydrogen atoms in the molecule could be located from a difference electron density map, they were placed at the respective calculated positions corresponding to a C—H distance of 1.08Å.[7] The parameters of the hydrogen atoms were not refined but their contribution to the structure factors were included during the refinement procedure. The hydrogen atoms were assigned isotropic temperature factors, same as the equivalent, isotropic temperature factor, U_{eq}, of the respective atom to which they are covalently bonded.

RESULTS AND DISCUSSION

Unlike in the crystal structure of Cu—OC_8H_{17},[1] in Cu—C_8H_{17}, the chemically identical halves of the molecule are related by crystallographic symmetry also. The

atomic numbering scheme is shown in Figure 2. Table II lists the positional and the U_{eq} values of the non-hydrogen atoms.[‖] The average of the U_{eq} values of the atoms of the crystallographically independent half of the core, viz., Cu, O(1), O(2), C(3) to C(5), is 0.042(2)Å^2. The average of the U_{eq} values for the phenyl rings on sides A and B (Figure 2) are 0.047(3) and 0.042(3)Å^2 respectively. As could be expected, the octyl chains have slightly higher thermal parameters. The U_{eq} values in the chains A and B average to 0.056(3) and 0.059(3)Å^2 respectively. There is, however, no evidence for any positional disorder of the type found in the crystal structure of Cu—OC_8H_{17}.[1]

The coordination around the copper atoms is square planar with the copper-oxygen distance averaging to 1.908(4)Å. As in the case of Pd—$C_{10}H_{21}$,[2] the special position occupied by the metal atom confers a strictly square planar character to the coordination polyhedron. Table III presents the bond lengths and bond angles. Within limits of experimental error, the molecular dimensions are normal. In Figure 2 the displacements, δ's, of the atoms from the least squares plane through the core (plane C hereafter) have been marked. It is found that the core is only nearly planar, with the displacement of the copper atom from plane C being −0.098Å. It is found that on moving away from the core of the molecule, the δ's increase, the value being the highest, viz., 2.016(8)Å, for the terminal atom C(19). It must be mentioned that the highest δ found in this crystal structure is higher than the corresponding values found in the crystal structures of Cu—OC_8H_{17}[1] and Pd—$C_{10}H_{21}$.[2] Therefore, it appears that in the crystal structure, the molecule of Cu—C_8H_{17} is less planar than the molecules of Cu—OC_8H_{17} and Pd—$C_{10}H_{21}$. The planar phenyl rings A and B are tilted with respect to plane C by 17 and 11° respectively. The corresponding values for the octyl chains are 16 and 12° respectively.

Figure 3 shows the conformation and the arrangement of the molecules in the plane perpendicular to the crystallographic *a*-axis. Both the octyl chains are fully extended in an all-trans conformation which resembles the model B given by Ohta *et al.*[12] In this conformation, the linear dimensions of the molecule calculated from the distances C(19) . . . C(33) and C(33) . . . C(19)′ are 30.4 and 9.7Å respectively. Here, the symbol ′ denotes the atom related by a centre of inversion. Figure 3 shows that whereas chain B is pointing towards the chain of a neighbouring molecule, chain A is oriented towards a core. Such an arrangement leads to interleaving of the chains of molecules related by unit cell translation along the *c*-direction. The molecular arrangement in the plane shown in Figure 3 is essentially layer like. Each molecule in the layer is surrounded by six others situated at $\pm\vec{c}$, $\pm(\vec{b}+\vec{c})$ and $\pm(\vec{b}+2\vec{c})$ and the interactions are essentially van der Waals' type. Layers of the type shown in Figure 3 are stacked periodically along the crystallographic *a*-axis to give rise to a columnar arrangement. The core of the molecule is tilted with respect to the column axis (which is the crystallographic *a*-axis) by 122°. In Figure 4, a schematic representation of the columnar arrangement of molecules is shown. Here, $\vec{n}$ represents the normal to plane C. The Cu . . . Cu distance along the column axis is 5.82Å. From Figure 3 it is also observed that the interior of each column comprising of the rigid cores of the molecules is surrounded by a fringe

[‖] A listing of the structure factors is available with the authors and can be obtained on request.

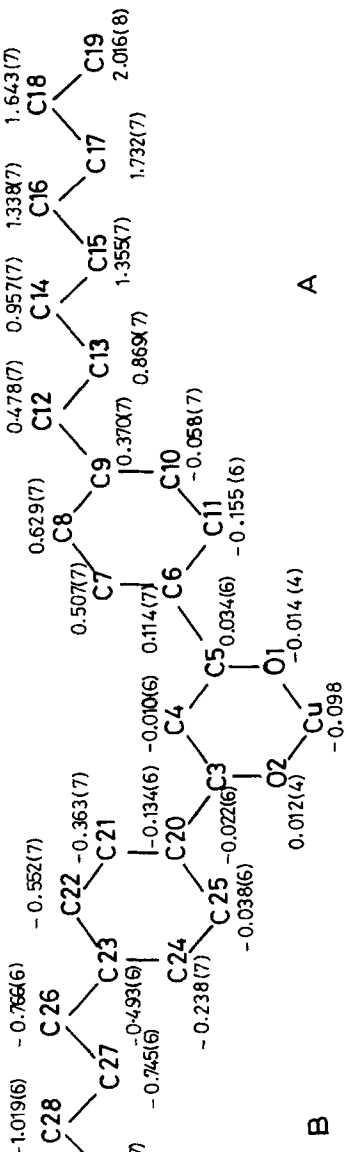

FIGURE 2 The displacement, δ, in Å of non hydrogen atoms from plane C.

TABLE II

Final fractional atomic coordinates and U_{eq}(Å^2)

Atom	X	Y	Z	U_{eq}
Cu	0.0000	0.0000	0.0000	0.0439(5)
O(1)	0.2644(8)	0.0546(3)	-0.0316(2)	0.046(2)
O(2)	0.0429(8)	0.1022(3)	0.1005(2)	0.046(2)
C(3)	0.216(1)	0.1695(4)	0.1291(3)	0.036(3)
C(4)	0.391(1)	0.1856(4)	0.0879(4)	0.041(3)
C(5)	0.402(1)	0.1298(4)	0.0097(3)	0.038(3)
C(6)	0.592(1)	0.1548(5)	-0.0328(3)	0.040(3)
C(7)	0.725(1)	0.2462(5)	-0.0078(4)	0.052(3)
C(8)	0.887(1)	0.2661(5)	-0.0519(4)	0.054(3)
C(9)	0.924(1)	0.1974(5)	-0.1214(4)	0.043(3)
C(10)	0.795(1)	0.1054(5)	-0.1446(4)	0.051(3)
C(11)	0.626(1)	0.0847(4)	-0.1022(4)	0.044(3)
C(12)	0.107(1)	0.2209(5)	-0.1667(4)	0.055(3)
C(13)	0.061(1)	0.1709(5)	-0.2564(4)	0.058(3)
C(14)	0.251(1)	0.1963(5)	-0.2995(4)	0.051(3)
C(15)	0.201(1)	0.1449(5)	-0.3903(4)	0.050(3)
C(16)	0.399(1)	0.1635(5)	-0.4331(4)	0.049(3)
C(17)	0.350(1)	0.1120(5)	-0.5238(4)	0.053(3)
C(18)	0.555(1)	0.1274(5)	-0.5648(4)	0.05?(3)
C(19)	0.505(2)	0.0744(5)	-0.6553(4)	0.072(4)
C(20)	0.220(1)	0.2304(4)	0.2160(3)	0.033(3)
C(21)	0.411(1)	0.2995(5)	0.2620(4)	0.047(3)
C(22)	0.411(1)	0.3474(5)	0.3427(4)	0.049(3)
C(23)	0.225(1)	0.3319(4)	0.3802(3)	0.035(3)
C(24)	0.038(1)	0.2658(5)	0.3338(3)	0.045(3)
C(25)	0.033(1)	0.2172(4)	0.2528(4)	0.044(3)
C(26)	0.247(1)	0.3847(4)	0.4690(3)	0.047(3)
C(27)	0.048(1)	0.3652(4)	0.5102(3)	0.039(3)
C(28)	0.092(1)	0.4244(4)	0.5994(3)	0.045(3)
C(29)	-0.102(1)	0.4081(5)	0.6447(3)	0.048(3)
C(30)	-0.049(1)	0.4683(5)	0.7336(4)	0.053(3)
C(31)	-0.243(1)	0.4559(5)	0.7797(4)	0.059(3)
C(32)	-0.191(2)	0.5187(6)	0.8669(4)	0.077(4)
C(33)	-0.387(2)	0.5083(7)	0.9118(5)	0.101(5)

TABLE III

Final bond lengths (Å) and bond angle (°)

Bond lengths			
Cu - O(1)	1.914(5)	C(3) - O(2) - Cu	125.9(4)
Cu - O(2)	1.902(3)	O(2) - C(3) - C(4)	125.1(6)
O(1) - C(5)	1.257(6)	O(2) - C(3) - C(20)	113.5(5)
O(2) - C(3)	1.276(7)	C(4) - C(3) - C(20)	121.4(5)
C(3) - C(4)	1.39(1)	C(3) - C(4) - C(5)	124.2(6)
C(3) - C(20)	1.516(7)	O(1) - C(5) - C(4)	124.8(6)
C(4) - C(5)	1.387(8)	O(1) - C(5) - C(6)	114.0(5)
C(5) - C(6)	1.508(9)	C(4) - C(5) - C(6)	121.2(5)
C(6) - C(11)	1.384(8)	C(11) - C(6) - C(7)	118.8(6)
C(6) - C(7)	1.390(9)	C(11) - C(6) - C(5)	117.9(6)
C(7) - C(8)	1.38(1)	C(7) - C(6) - C(5)	123.2(6)
C(8) - C(9)	1.380(9)	C(8) - C(7) - C(6)	120.3(7)
C(9) - C(10)	1.39(1)	C(9) - C(8) - C(7)	121.9(7)
C(9) - C(12)	1.51(1)	C(8) - C(9) - C(10)	117.4(7)
C(10) - C(11)	1.39(1)	C(8) - C(9) - C(12)	120.4(6)
C(12) - C(13)	1.501(9)	C(10) - C(9) - C(12)	122.2(6)
C(13) - C(14)	1.52(1)	C(11) - C(10) - C(9)	121.6(7)
C(14) - C(15)	1.522(9)	C(10) - C(11) - C(6)	120.0(6)
C(15) - C(16)	1.53(1)	C(13) - C(12) - C(9)	116.3(6)
C(16) - C(17)	1.522(9)	C(12) - C(13) - C(14)	114.5(6)
C(17) - C(18)	1.52(1)	C(13) - C(14) - C(15)	113.6(6)
C(18) - C(19)	1.521(9)	C(14) - C(15) - C(16)	113.9(6)
C(20) - C(25)	1.38(1)	C(17) - C(16) - C(15)	114.0(6)
C(20) - C(21)	1.408(8)	C(16) - C(17) - C(18)	113.2(6)
C(21) - C(22)	1.383(9)	C(19) - C(18) - C(17)	113.0(6)
C(22) - C(23)	1.39(1)	C(25) - C(20) - C(21)	118.0(6)
C(23) - C(24)	1.375(8)	C(25) - C(20) - C(3)	119.6(5)
C(23) - C(26)	1.503(7)	C(21) - C(20) - C(3)	122.4(5)
C(24) - C(25)	1.386(8)	C(22) - C(21) - C(20)	119.4(6)
C(26) - C(27)	1.51(1)	C(21) - C(22) - C(23)	122.4(6)
C(27) - C(28)	1.521(7)	C(24) - C(23) - C(22)	117.3(6)
C(28) - C(29)	1.52(1)	C(24) - C(23) - C(26)	124.4(6)
C(29) - C(30)	1.520(8)	C(22) - C(23) - C(26)	118.2(6)
C(30) - C(31)	1.52(1)	C(23) - C(24) - C(25)	121.4(6)
C(31) - C(32)	1.503(9)	C(20) - C(25) - C(24)	121.3(6)
C(32) - C(33)	1.51(1)	C(23) - C(26) - C(27)	118.1(5)
		C(26) - C(27) - C(28)	112.4(5)
		C(27) - C(28) - C(29)	115.1(5)
Bond angles		C(30) - C(29) - C(28)	113.0(5)
O(2) - Cu - O(1)	92.8(2)	C(29) - C(30) - C(31)	114.1(6)
C(5) - O(1) - Cu	126.7(4)	C(32) - C(31) - C(30)	113.4(6)
		C(31) - C(32) - C(33)	113.3(7)

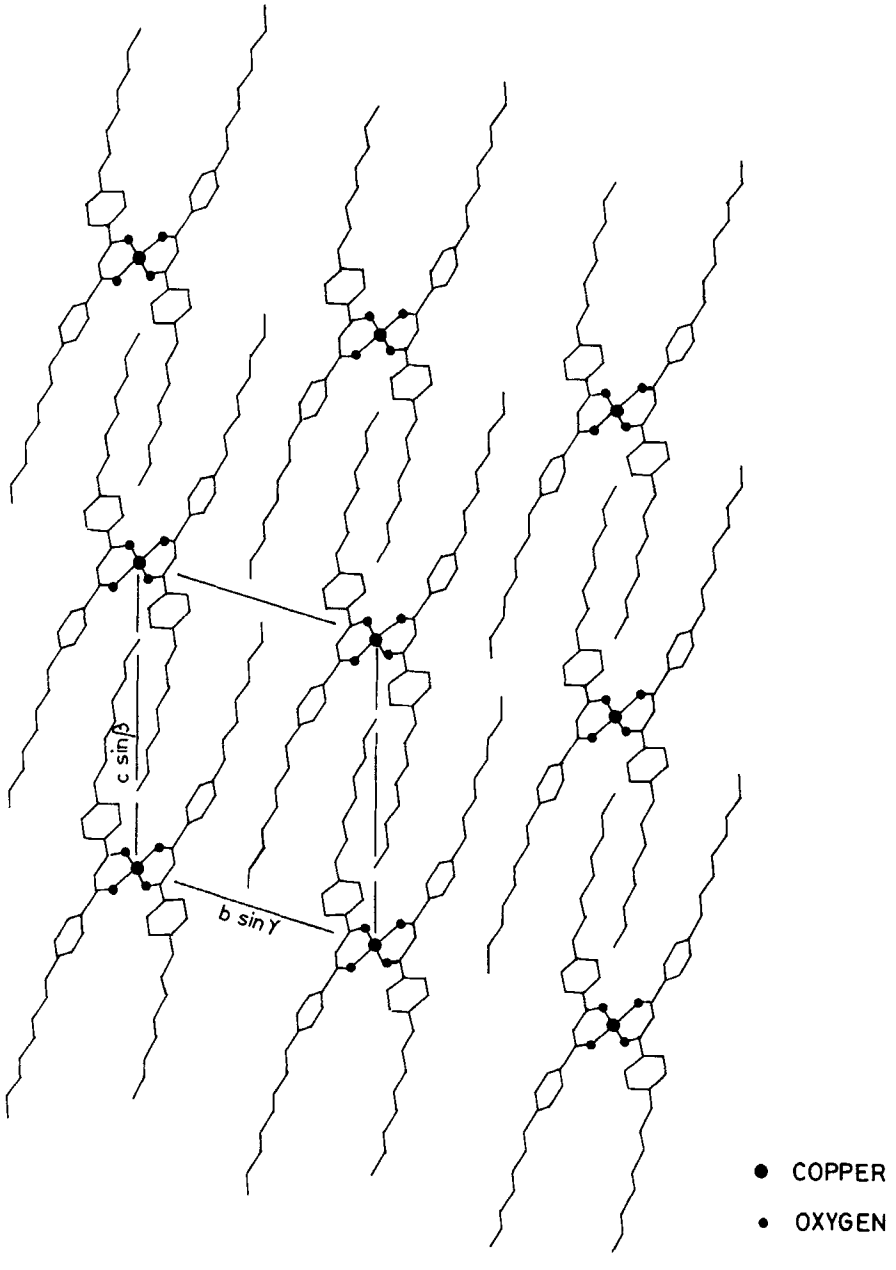

FIGURE 3 Molecular arrangement in the plane perpendicular to *a*-axis.

made up of flexible octyl chains. Fringes of the neighbouring columns exhibit conspicuous interpenetration.

Another conspicuous feature in this crystal structure concerns the intermolecular, non-bonded interactions. Within a layer, the non-bonded intermolecular interac-

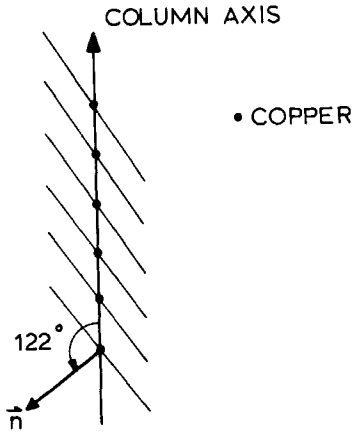

FIGURE 4 Schematic representation of the tilted columnar arrangement. $\hat{n}$ represents the normal to plane C.

tions are found to be of the chain-chain and chain-phenyl ring type. In contrast, along the axis of the column, the predominant non-bonded interactions are of the core-phenyl ring type.

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