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Short Communication

Crystal and molecular structure of the mesogenic complex bis[*N*-4-(n-propyl)-phenyl-4'-(n-dodecyloxy)salicylidene-iminato]copper(II)

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Abstract

The X-ray crystal structure of the complex $(C_3H_7L)_2Cu$, C_3H_7L = *N*-4(n-propyl)phenyl-4'-(n-dodecyloxy)salicyldene-aminato, is reported. Crystals were monoclinic *C2/c* space group, with $a = 53.76(3)$, $b = 8.540(4)$, $c = 12.027(6)$ Å, $\beta = 94.89(4)°$ and $Z = 4$. The structure was refined to $R = 0.079$ for 145 parameters using 1314 reflections with $I > 3\sigma(I)$. The compound consists of C_3H_7L ligand moieties bonded to copper atoms in a *trans* geometry. $(C_3H_7L)_2Cu$ is a mesogenic compound which shows an enantiotropic smectic A phase between 112 and 152 °C; the analogies with respect to the structure found in such a mesophase are described.

Introduction

Several copper coordination compounds whose ligands are salicylideneamine derivatives display liquid crystalline properties [1, 2]. The molecular packing exhibited by the different mesophases of some of them has been investigated by X-ray diffraction measurements carried on powder samples [3–12]. Thus, as an example, the smectic A (S_A) mesophase displayed by the *N*-(4-dodecyloxysalicylidene)-4'-alkylanilines species $(R_nL)_2Cu$ was found to consist of a two dimensional array of interdigitated molecules. Herein we report on the X-ray analysis carried on the homologous 4'-*n*-propyl complex, $(C_3H_7L)_2Cu$, as a single crystal. $(C_3H_7L)_2Cu$ is a mesogenic compound which shows a monotropic solid–solid transition at 89 °C and an enantiotropic smectic A phase between 112 and 152 °C [13].

X-ray data collection and structure refinement

The $(C_3H_7L)_2Cu$ complex was synthesized according to the previously reported procedure [13]. Crystals suitable for X-ray analysis have been obtained as dark brown platelets by slow evaporation of a 3:1 diethyl ether/ethanol solution. Diffraction data were collected on a Siemens R3m/V automatic four-circle diffractometer, using graphite-monochromated Mo Kα radiation. Crystal data for $C_{56}H_{80}N_2O_4Cu$: $M = 908.8$, $a = 53.76(3)$, $b = 8.540(4)$, $c = 12.027(6)$ Å, $\beta = 94.89(4)°$; $V = 5502(5)$ Å^3, $Z = 4$, $D_{calc} = 1.097$ g cm^{-3}, $F(000) = 1964$, Mo Kα radiation ($\lambda = 0.71073$); μ(Mo Kα) $= 4.37$ cm^{-1}, monoclinic, space group *C2/c*. A crystal of $0.50 \times 0.45 \times 0.03$ mm was used to collect 2774 reflections in the range $0 < 2\theta < 45°$. Only 1314 independent reflections were observed ($R_{int} = 0.0115$). Lorentz-polarization and ψ-scan absorption corrections [14] were applied to the intensity data. The structures were solved by standard Patterson methods and subsequently completed by Fourier recycling. Only Cu, N and O atoms were refined anisotropically. All hydrogen atoms were set in calculated positions and refined as riding atoms. A common thermal parameter was assigned to all hydrogen atoms. The final R value was 0.079, $R_w = 0.084$ (weighting scheme $w = 1.0000/[\sigma^2(F_o) + 0.001885F_o^2]$), $S = 1.88$.

Solutions and refinements were performed with the SHELXTL-PLUS system [15]. The final geometrical calculations were carried out with the PARST program [16]. The graphical manipulations were performed using the XP utility of the SHELXTL-PLUS system. See also 'Supplementary material'.

Results and discussion

The molecular structure of the $(C_3H_7L)_2Cu$ complex with the atom labelling scheme is shown in Fig. 1. Table 1 lists selected bond lengths and angles. The structure consists of two *N*-4-(n-propyl)phenyl-4'-(*n*-dodecyloxy)salicylideneiminato moieties (C_3H_7L) bonded to the copper atom via nitrogen and oxygen atoms. The two pairs of Cu–O and Cu–N lengths are similar to those in related complexes [4, 17–21]; they are in a mutually *trans* geometry so that the two C_3H_7L fragments are oriented head-to-tail. The coordination about the copper atom is quite usual for compounds of this type [4, 17–21] being square planar distorted towards a tetrahedral pattern. The N(1)–Cu(1)–N(2) and O(1)–Cu–O(2) angles are 156.0(1) and 148.9(1)°, respectively.

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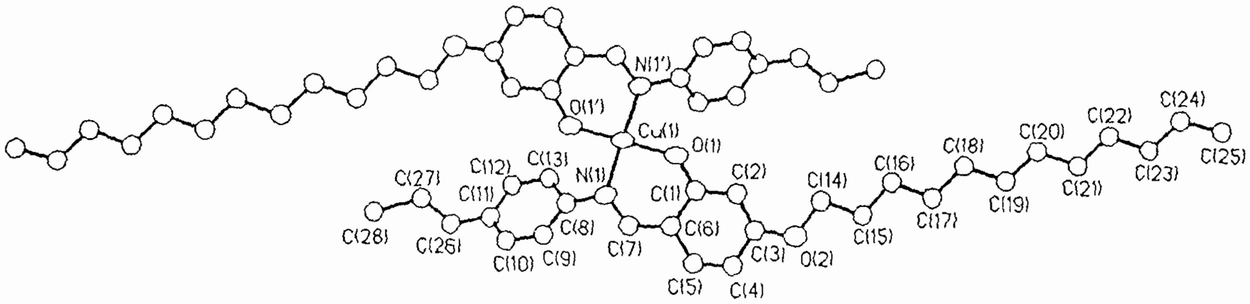

Fig. 1. View of the $(C_3H_7L)_2Cu$ complex, with the atom numbering scheme. All carbon atoms are drawn with uniform arbitrarily sized circles. Thermal ellipsoids of the remaining atoms are plotted at the 30% probability level. Hydrogen atoms are omitted.

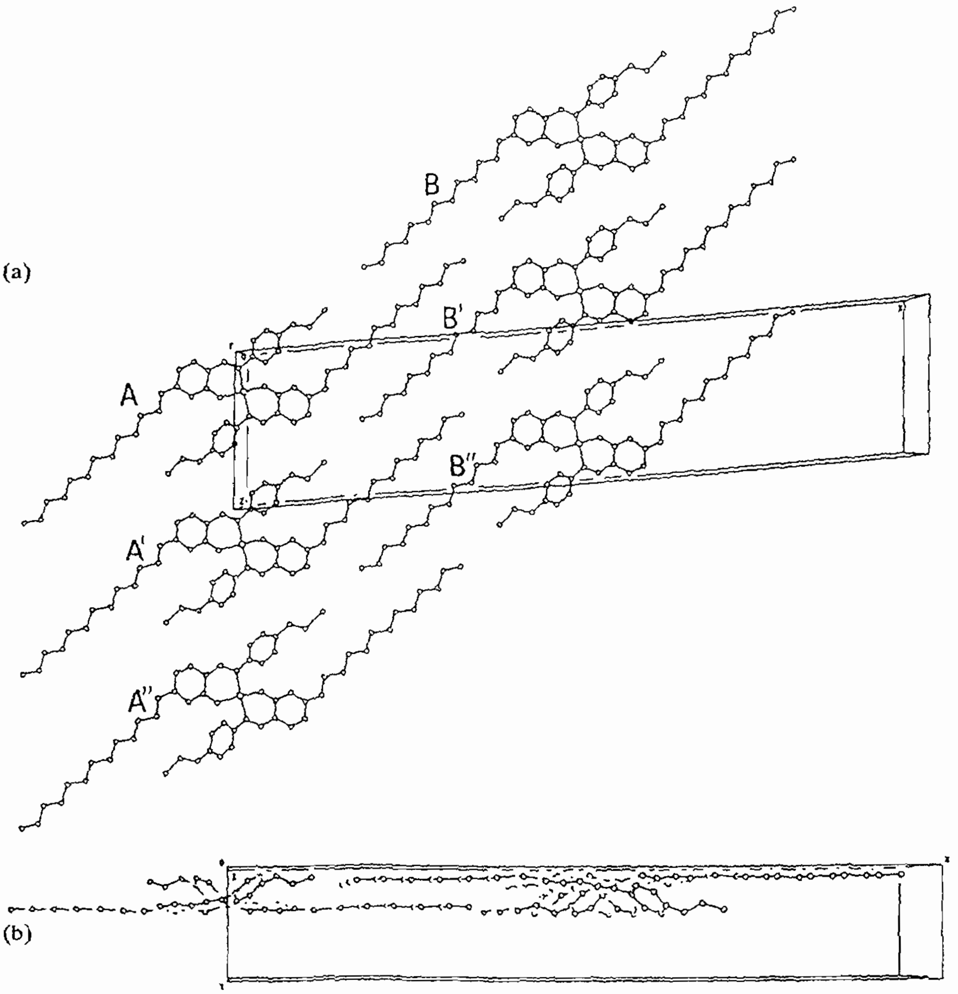

Fig. 2. The molecular array of two different families of molecules disposed on parallel planes: (a) view along *b* axis; (b) view along *c* axis.

The atoms which provide the metal containing rings are approximately coplanar, with C(1) at 0.1 Å above the N(1),C(7),C(6),C(1),O(1) mean plane. With reference to this plane, the N-bonded phenyl ring is tilted by 47.7(4)° while the C(1),C(2),C(3),C(4),C(5),C(6) plane is tilted by 8.3°. The aliphatic chains adopt an all-*trans* conformation. In this way, $(C_3H_7L)_2Cu$ conforms to similar complexes.

The molecular geometry is dictated by the copper coordination sphere; however, in spite of the distorted tetrahedral geometry it should be pointed out both the ends of the dodecyloxy chains (from C(14) to C(25)

TABLE 1. Selected interatomic distances (Å) and bond angles (°) for $C_{56}H_{80}N_2O_4Cu$ with e.s.d.s in parentheses

Cu(1)–O(1)	1.887(7)	Cu(1)–N(1)	1.973(8)
O(1)–C(1)	1.343(12)	C(1)–C(6)	1.420(15)
C(6)–C(7)	1.406(15)	N(1)–C(7)	1.290(13)
O(1)–Cu(1)–N(1)	94.9(3)	O(1)–Cu(1)–O(1′)	148.9(5)
N(1)–Cu(1)–O(1′)	91.5(3)	N(1)–Cu(1)–N(1′)	156.2(6)
Cu(1)–O(1)–C(1)	128.4(7)	O(1)–C(1)–C(2)	119.7(10)
O(1)–C(1)–C(6)	119.1(9)	C(2)–C(1)–C(6)	121.0(9)
C(1)–C(6)–C(5)	115.7(9)	C(1)–C(6)–C(7)	125.3(9)
C(5)–C(6)–C(7)	118.6(9)	N(1)–C(7)–C(6)	129.2(10)
Cu(1)–N(1)–C(7)	120.7(7)	Cu(1)–N(1)–C(8)	121.2(6)
C(7)–N(1)–C(8)	118.1(9)		

or from C(14)′ to C(25)′) lie almost on the same plane (the molecular plane, as indicated in Fig. 2(b)). The copper atom is 0.365(3) Å above such a plane.

An understanding of the way in which the molecules are arranged in the crystal may be of interest in relation to the liquid crystal properties of the compound. The molecular packing is illustrated in Fig. 2. It may be described considering the set of molecules A, A′, A″ (related by a translation along z) and the neighbouring set of molecules B, B′, B″ (also related by a translation along z). As shown in Fig. 2(a), molecule B′ is obtained from A by inversion and C-centering (symmetry operation: $\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$). The mutual arrangement of the two sets of molecules is such that they are interdigitated with facing of parts of the long aliphatic chains ($C_{14}H_{25}O$). In Fig. 2(b) it may be seen that, because of the symmetry, the molecular planes of molecules A, A′, A″ are all coplanar; the molecular planes of molecules B, B′, B″ are also coplanar, but they are not coplanar with those of molecules A, A′, A″. Since molecules B are inverted with respect to molecules A, the pairing of the two sets of molecules occurs face to face (Fig. 2(b)). The interdigitation is such that the distances between the chains are equal. Indeed the distance C(22)...C(24)′ of 4.29(2) Å between molecules A and B is equal to the distance C(19)...C(19′) = 4.30(1) Å between molecules A and B′.

Concluding, the single crystal X-ray analysis, performed on $(C_3H_7L)_2Cu$ gives a molecular packing consisting of a layered structure containing interdigitated molecules. A similar structure was previously proposed for the S_A phase displayed by the whole $(C_nH_{2n+1}L)_2Cu$ mesogenic series [11]. Therefore in the present case both the solid and S_A phase display the same structural features.

Supplementary material

Table of crystallographic data and tables with the final atomic coordinates for the non-hydrogen atoms and the hydrogen atoms, the total bond distances (Å) and angles (°), the thermal parameters, least-squares planes and a list of calculated and observed structure factors are available from the authors on request.

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References

1 A.M. Giroud-Godquin and P.M. Maitlis, *Angew. Chem., Int. Ed. Engl., 30* (1991) 375.
2 P. Espinet, M.A. Esteruelas, L.A. Oro, J.L. Serrano and E. Sola, *Coord. Chem. Rev., 117* (1992) 215.
3 E. Bui, J.P. Bayle, F. Perez, L. Liebert and J. Courtieu, *Liq. Cryst., 8* (1990) 513.
4 A. Roviello, S. Sirigu, P. Iannelli and A. Immirzi, *Liq. Cryst., 3* (1988) 115.
5 U. Caruso, A. Roviello and S. Sirigu, *Liq. Cryst., 3* (1988) 1515.
6 M. Marcos, P. Romero, J.L. Serrano, J. Barberà and A.M. Levelut, *Liq. Cryst., 7* (1990) 251.
7 U. Caruso, A. Roviello and A. Sirigu, *Liq. Cryst., 7* (1990) 421.
8 U. Caruso, A. Roviello and S. Sirigu, *Liq. Cryst., 7* (1990) 431.
9 J. Barberà, A.M. Levelut, M. Marcos, P. Romero and J.L. Serrano, *Liq. Cryst., 10* (1991) 119.
10 M. Ghedini, S. Armentano, R. Bartolino, G. Torquati and F. Rustichelli, *Solid State Commun., 64* (1987) 1191.
11 G. Torquati, O. Francescangeli, M. Ghedini, S. Armentano, F.P. Nicoletta and R. Bartolino, *Il Nuovo Cimento, 12D* (1990) 1363.
12 A.M. Levelut, M. Ghedini, R. Bartolino, F.P. Nicoletta and F. Rustichelli, *J. Phys. (F), 50* (1989) 113.
13 M. Ghedini, S. Morrone, D. Gatteschi and C. Zanchini, *Chem. Mater., 3* (1991) 752.
14 A.C.T. North, D.C. Phillips and F.S. Mathews, *Acta Crystallogr., Sect. A, 24* (1968) 351.
15 *SHELXL PLUS*, Version 3.4, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1989.
16 M. Nardelli, *Comput. Chem., 7* (1983) 95.
17 N. Hoshino, H. Murakami, Y. Matsuaga, T. Inabe and Y. Maruyama, *Inorg. Chem., 29* (1990) 1177.
18 M. Carotenuto, P. Iannelli, A. Immirzi, U. Caruso, A. Roviello and A. Sirigu, *Acta Crystallogr., Sect. C, 4* (1990) 2031.
19 A.P. Polishchuk, M.Yu. Antipin, T.V. Timofeeva, Yu.T. Struchkov, Yu.G. Galyametdinov and I.V. Ovchinnikov, *Kristallografiya, 31* (1986) 466.
20 A.P. Polishchuk, M.Yu. Antipin, T.V. Timofeeva, Yu.T. Struchkov, Yu.G. Galyametdinov and I.V. Ovchinnikov, *Kristallografiya, 9* (1980) 91.
21 A.P. Polishchuk, M.Yu. Antipin, R.G. Gerr, T.V. Timofeeva, Yu.T. Struchkov, Yu.G. Galyametdinov and I.V. Ovchinnikov, *Kristallografiya, 34* (1989) 122.