Bis[2-(ethylimino-κN-methyl)-5-(hexyloxyphenoxycarbonyl)phenolato-κO]copper(II)

By M. Carotenuto, P. Iannelli and A. Immirzi

*Dipartimento di Fisica, Università di Salerno, I-84100 Salerno, Italy*

and U. Caruso, A. Roviello and A. Sirigu

Dipartimento di Chimica, Università di Napoli, Via Mezzocannone 4, I-80134 Napoli, Italy

Abstract. $[Cu(C_{22}H_{26}NO_4)_2]$, $M_r = 800 \cdot 5$, is a bis-coordinate complex $Cu^{II}L^2$ where the bidentate L ligand is an N-ethylsalicylideneaminato derivative having the long chain substituent $OCOC_6H_4O(CH_2)_5CH_3$ in the *para* position with respect to C=N. This compound is crystalline at room temperature and melts giving monotropic nematic mesomorphism. Crystals are triclinic, $P\bar{1}$, $a = 10 \cdot 866\,(5)$, $b = 11 \cdot 307\,(4)$, $c = 8 \cdot 768\,(5)$ Å, $\alpha = 106 \cdot 37\,(5)$, $\beta = 90 \cdot 32\,(4)$, $\gamma = 97 \cdot 34\,(6)°$, $V = 1024\,(2)$ Å^3, $Z = 1$, D_m (flotation) $= 1 \cdot 30\,(5)$, $D_x = 1 \cdot 297$ g cm^{-3}, $\lambda(Cu\,K\alpha) = 1 \cdot 54178$ Å, $\mu = 12 \cdot 1$ cm^{-1}, $F(000) = 423$, room temperature, $R = 0 \cdot 085$ for 3033 observed independent reflections. The complex is *trans* square planar. The molecule has C_i symmetry and a flattened shape. The dihedral angle between the planar salicylideneaminato group and the N-bonded ethyl group is $89 \cdot 3\,(8)°$. The planar salicylideneaminato group and the benzoyloxy group are twisted by $57 \cdot 1°$.

Introduction. The title compound (which has the chemical structure shown in the scheme) is mesogenic. Several other related mesogenic salicylideneaminato copper(II) and palladium(II) complexes have recently been reported (Caruso, Roviello & Sirigu, 1988), a second long chain group (p-alkoxy or p-alkoxyloxy benzene with linear alkyls) replacing C_2H_5.

$R_1 = C_2H_5$ $R_2 = OCOC_6H_4O(CH_2)_5CH_3$
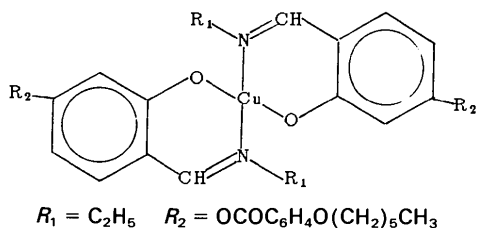
In the search for possible correlations between molecular structure, packing and liquid crystalline behaviour, the crystal structure of the complexes with $R_1 = C_6H_4O(CH_2)_5CH_3$ and $R_2 = O(CH_2)_6CH_3$ coordinated to copper(II) and to palladium(II) were

determined (Iannelli, Immirzi, Roviello & Sirigu, 1988; Iannelli, Immirzi, Caruso, Roviello & Sirigu, 1989). The smectic nature of the mesophase and the measured smectic interlayer distance was found to be related to the presence in the crystal phase of layers of comparable thickness containing molecules packed with their elongation axes parallel to each other.

The title compound is one of a series of homologues exhibiting mesogenic behaviour whose chemical structure was designed by increasing the elongation of the rigid part of the molecule with the purpose of favouring the onset of nematic rather than smectic mesomorphism. Nematic mesomorphism has actually been observed either as the only mesophase occurring or in addition to the smectic one (Caruso, Roviello & Sirigu, 1989).

Experimental. The title compound was prepared according to a procedure described elsewhere (Caruso, Roviello & Sirigu, 1989). Single crystals suitable for X-ray diffraction measurements were crystallized from chloroform/ethanol mixtures. Crystal: $0 \cdot 8 \times 0 \cdot 5 \times 0 \cdot 02$ mm. X-ray-diffraction measurements were performed on a Philips PW1100 automated single-crystal diffractometer, Ni-filtered $Cu\,K\alpha$ radiation, 2θ–ω scan mode, $\sin\theta/\lambda \leq 0 \cdot 562$ Å^{-1}, $-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $0 < l \leq 9$. Unit-cell dimensions from 25 reflections ($6 \cdot 5 < \theta < 14 \cdot 2°$). Two standard reflections monitored every two hours showed only random deviations. 3033 independent reflections were measured of which 2838 having $I > 3\sigma(I)$ were considered for structure refinement. Corrections for Lorentz and polarization factors were applied. Absorption correction was also applied according to the method of North, Phillips & Mathews (1968); min., max. trasmission coefficients $0 \cdot 65$, $1 \cdot 00$. All calculations were performed using the *SHELX* package (Sheldrick, 1976). The crystal structure was determined starting from the Cu-atom position and by repeated application of the Fourier method. For the refinement, H atoms were placed in calculated positions according to standard geometries, and attributing a single U_{iso} value [final value

$$[Cu(C_{22}H_{26}NO_4)_2]$$

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
Cu	0·0000	0·0000	0·0000	0·0554 (9)
O1	0·1145 (3)	0·0362 (5)	−0·1468 (5)	0·070 (5)
N	0·1367 (4)	−0·0012 (4)	0·1516 (5)	0·047 (4)
C1	0·2520 (5)	0·0373 (5)	0·1376 (6)	0·048 (4)
C2	0·3035 (5)	0·0828 (5)	0·0110 (6)	0·041 (4)
C3	0·4301 (5)	0·1289 (6)	0·0229 (6)	0·054 (5)
C4	0·4875 (5)	0·1730 (6)	−0·0935 (7)	0·058 (5)
C5	0·4159 (5)	0·1688 (5)	−0·2247 (6)	0·048 (4)
C6	0·2918 (5)	0·1252 (6)	−0·2432 (6)	0·051 (5)
C7	0·2322 (5)	0·0800 (5)	−0·1242 (6)	0·048 (4)
O2	0·4655 (3)	0·2200 (4)	−0·3442 (4)	0·055 (3)
C8	0·5642 (5)	0·1714 (5)	−0·4235 (6)	0·046 (4)
O3	0·6093 (4)	0·0889 (4)	−0·3980 (5)	0·057 (3)
C9	0·6037 (5)	0·2371 (5)	−0·5432 (6)	0·043 (4)
C10	0·5439 (5)	0·3304 (5)	−0·5692 (7)	0·052 (4)
C11	0·5843 (6)	0·3905 (6)	−0·6808 (7)	0·057 (5)
C12	0·6884 (6)	0·3545 (6)	−0·7674 (7)	0·055 (4)
C13	0·7482 (5)	0·2595 (6)	−0·7432 (7)	0·055 (5)
C14	0·7072 (5)	0·2027 (5)	−0·6313 (7)	0·051 (4)
O4	0·7349 (4)	0·4058 (4)	−0·8806 (5)	0·074 (4)
C15	0·6800 (9)	0·5094 (8)	−0·9057 (10)	0·11 (1)
C16	0·7628 (14)	0·5685 (9)	−1·0170 (13)	0·21 (3)
C17	0·7689 (16)	0·4810 (11)	−1·1742 (14)	0·26 (3)
C18	0·8627 (13)	0·5330 (13)	−1·2801 (16)	0·21 (2)
C19	0·8277 (13)	0·6464 (11)	−1·3118 (15)	0·18 (2)
C20	0·8889 (11)	0·6731 (11)	−1·4579 (12)	0·15 (1)
C21	0·1091 (6)	−0·0471 (7)	0·2915 (7)	0·067 (7)
C22	0·0884 (8)	−0·1858 (8)	0·2404 (11)	0·096 (8)

Table 2. Relevant bond distances (Å) and angles (°) with e.s.d.'s in parentheses

Cu—O1	1·886 (4)	Cu—N	1·992 (4)
N—C1	1·291 (6)	N—C21	1·479 (7)
O1—C7	1·305 (6)	C1—C2	1·437 (7)
C2—C3	1·399 (7)	C3—C4	1·377 (7)
C4—C5	1·372 (8)	C5—C6	1·367 (7)
C6—C7	1·412 (7)	C2—C7	1·403 (7)
C5—O2	1·412 (6)	O2—C8	1·371 (6)
C8—O3	1·181 (6)	C8—C9	1·484 (7)
C9—C10	1·377 (8)	C9—C14	1·402 (7)
C10—C11	1·384 (8)	C11—C12	1·405 (8)
C14—C13	1·364 (8)	C13—C12	1·388 (8)
C12—O4	1·353 (6)	O4—C15	1·449 (8)
C15—C16	1·560 (8)	C16—C17	1·460 (9)
C17—C18	1·553 (8)	C18—C19	1·480 (8)
C19—C20	1·534 (8)	C21—C22	1·491 (10)
N—Cu—O1	91·5 (2)	C7—O1—Cu	129·3 (3)
C1—N—Cu	124·0 (4)	C21—N—Cu	120·2 (3)
C2—C1—N	126·8 (5)	C7—C2—C1	122·4 (5)
C7—C2—C3	119·4 (5)	C4—C3—C2	122·2 (5)
C5—C4—C3	117·3 (5)	C6—C5—C4	123·4 (5)
O2—C5—C4	120·8 (5)	C7—C6—C5	119·6 (5)
C2—C7—O1	123·5 (5)	C6—C7—C2	118·1 (5)
C8—O2—C5	117·9 (4)	O3—C8—O2	123·7 (5)
C9—C8—O2	110·2 (5)	C10—C9—C8	122·7 (5)
C14—C9—C10	119·4 (5)	C11—C10—C9	121·0 (5)
C12—C11—C10	118·6 (6)	C13—C12—C11	120·7 (5)
O4—C12—C11	123·6 (6)	C14—C13—C12	119·5 (5)
C13—C14—C9	120·8 (5)	C15—O4—C12	118·2 (5)
C16—C15—O4	109·1 (6)	C17—C16—C15	111·8 (8)
C18—C17—C16	112·5 (9)	C19—C18—C17	112·1 (8)
C20—C19—C18	112·8 (7)	C22—C21—N	109·5 (6)

0·205 (12) Å^2]. Full-matrix least-squares procedure minimizing $\Sigma_i w_i(F_{obs,i} - F_{calc,i})^2$ with unitary w_i's, anisotropic parameters for all non-H atoms. Final R, wR and S values are 0·085, 0·085 and 1·4, respectively. Max. $\Delta/\sigma = 0·2$; max., min. heights in final difference electron-density map were 1·12, −0·57 e Å^{-3}. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1974).

Discussion. Atomic coordinates and equivalent isotropic thermal vibration parameters are listed in Table 1.* Bond lengths and angles are listed in Table 2, while Fig. 1 shows the molecular model. No significant deviations from expected values were observed for bond lengths and angles. The relevant aspects of the crystal packing are shown in Fig. 2.

The salicylideneaminato group is planar (within 0·08 Å), and its least-squares plane is almost coincident with the least-squares coordination plane [dihedral angle 5·3 (8)°]. The N-bonded ethyl group has its terminal C atom out of the plane of the salicylideneaminato group with C22 close to C1 (3·24 Å)

and O1 (3·18 Å). If the torsion angle about the N—C21 bond (actually 103°), is varied systematically, one observes that either the C22···C1 or the C22···O1 distance becomes shorter. So the observed conformation of the ethyl group is justified by the intramolecular interactions only and should be retained also in the liquid crystalline state.

The benzoyloxy group and the COO group are almost coplanar (r.m.s.d. from the least-squares plane for the nine atoms C9, C10, C11, C12, C13, C14, C8, O3 and O2 is 0·02 Å) but this plane is twisted with respect to the salicylic aromatic ring by 57·1° (the r.m.s.d. from the least-squares plane for the seven atoms C2, C3, C4, C5, C6, C7 and O2 is 0·02 Å). This twisted geometry is justified by intramolecular factors only, since the C8=O3 double bond is conjugated to the benzoyloxy group but not to the salicylic group and the untwisted geometry would imply a severe contact between O3 and the H atom bonded to C4 or C6.

Only molecular packing reasons can be responsible for the non-all-trans conformations taken by the alkoxy terminal chains. Two gauche bonds, viz C15—C16 and C17—C18, allow the alkoxy chain to keep its elongation axis collinear with the 4-benzoyloxysalicylindeneaminato ligand.

The molecules, which by requirement of the space group are all related by rigid translation, pack in a sort of imbricated pattern. The major elongation axis (i.e. the major axis of the central ellipsoid of inertia

of the molecule calculated considering all non-H atoms with equal weight) makes angles 54·5, 61·5 and 137·1° with the *a*, *b* and *c* edges, respectively.

The six molecules having the elongation axis closest to that of any reference molecule are the ones obtained by translations ± *a*, ± *b* and ± *c*. These molecules have axis-to-axis orthogonal distances
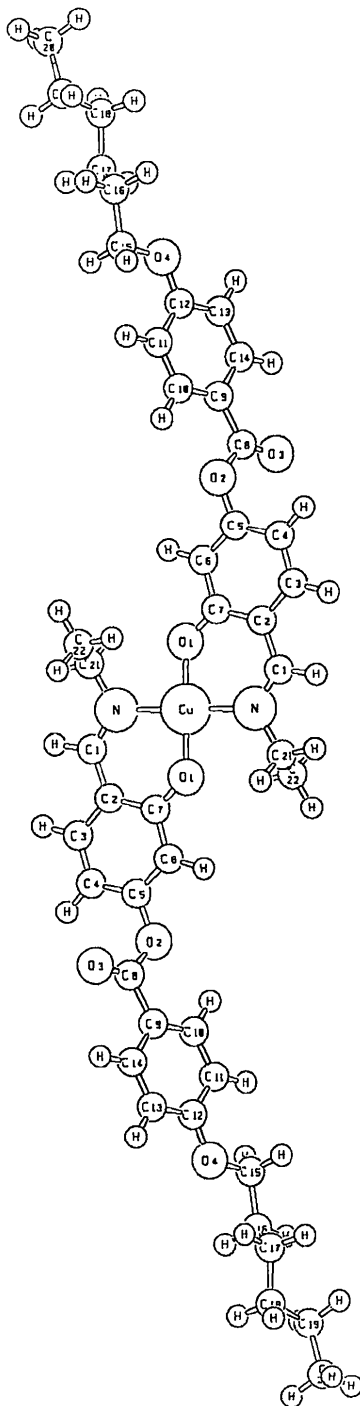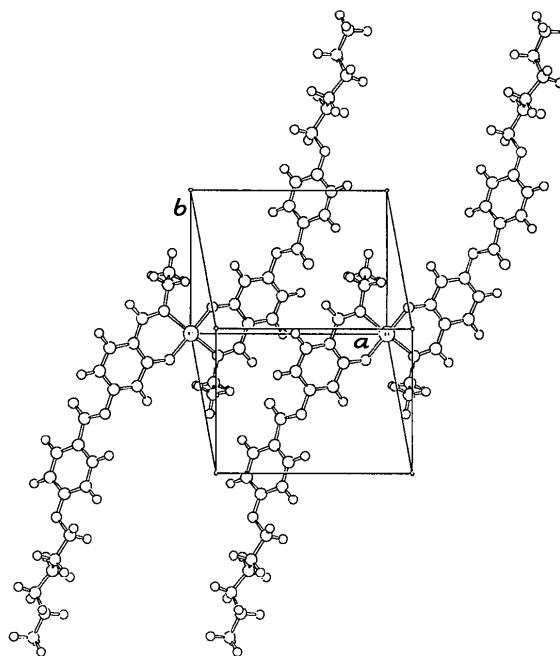

Fig. 1. Molecular drawing of the title compound.

Fig. 2. Packing of molecules in the crystallographic *xy* plane. For the sake of clarity only two molecules are drawn.

5·40, 6·31 and 5·97 Å, respectively and are shifted along the axis by ± 9·94, ± 8·85 and ± 6·43 Å. Smaller shifts (< 1 Å) relate molecules translated by ± (*b* + *c*) or ± (*a* + *c*), but axis-to-axis distances are somewhat larger (12·19 and 13·92 Å). The crystal packing does not show layers of parallel unshifted molecules, and appears a coherent precursor of the actual liquid crystal phase which is nematic and not smectic.

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