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2,3,7,8,12,13,17,18-Octaethyl-5-formyl-10-[2,2-bis(benzyloxycarbonyl)vinyl]-porphinatocopper(II)

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Abstract. $C_{55}H_{60}N_4O_5Cu$, triclinic, $P\bar{1}$, $a = 13{\cdot}441$ (2), $b = 14{\cdot}246$ (8), $c = 13{\cdot}220$ (3) Å, $\alpha = 96{\cdot}92$ (4), $\beta = 105{\cdot}65$ (2), $\gamma = 84{\cdot}85$ (4)°, $M_r = 920{\cdot}7$, $Z = 2$, $D_x = 1{\cdot}26$ g cm^{-3}. Very large distortions from planarity are observed in the porphyrin skeleton, in particular at the methine bridges, which are alternately 0·41–0·54 Å above and below the N atom plane. The Cu—N distances show a very significant spread [1·96, 2·02, 1·92, 2·05 (1) Å]. The phenyl ring of the *Z*-configurated ester group of the C(10) substituent is sited above and approximately perpendicular (86·5°) to the ligand field at the central Cu^{2+} ion.

Introduction. Cell dimensions were determined by a least-squares fit to settings for 15 reflexions ($\pm hkl$) on a Syntex $P2_1$ four-circle diffractometer [λ(Mo $K\alpha$) = 0·71069 Å]. Intensity measurements were carried out in the θ–2θ mode ($3{\cdot}0 \leq 2\theta \leq 45{\cdot}0°$) with graphite-monochromated Mo $K\alpha$ radiation, at scan speeds varying linearly between 2·93° min^{-1} (150 c.p.s. and below) and 6·51° min^{-1} (4000 c.p.s. and above). Scan and background times were equal. Lorentz and polarization corrections were applied but no absorption correction [μ(Mo $K\alpha$) = 4·6 cm^{-1}] was made. After application of the acceptance criterion $I \geq 2{\cdot}5\sigma(I)$,

Table 1. *Positional parameters* ($\times 10^4$)

	x	*y*	*z*
Cu	8018 (1)	5131 (1)	8960 (1)
N(23)	8211 (8)	3774 (8)	8881 (9)
C(11)	7759 (9)	3074 (11)	8157 (11)
C(12)	8117 (11)	2110 (9)	8414 (11)
C(13)	8870 (10)	2257 (11)	9329 (11)
C(14)	8903 (12)	3240 (11)	9626 (13)
C(15)	9454 (10)	3588 (10)	10594 (12)
N(24)	8792 (6)	5271 (9)	10531 (7)
C(16)	9347 (8)	4488 (11)	11013 (10)
C(17)	9712 (10)	4851 (11)	12117 (12)
C(18)	9399 (11)	5749 (11)	12258 (11)
C(19)	8743 (11)	6112 (12)	11211 (11)
C(20)	8306 (11)	6959 (9)	10965 (12)
N(21)	7750 (7)	6507 (8)	9047 (10)
C(1)	7824 (10)	7149 (13)	9895 (14)
C(2)	7462 (11)	8089 (10)	9681 (14)
C(3)	7193 (12)	8074 (11)	8618 (15)
C(4)	7362 (10)	7102 (13)	8249 (13)
C(5)	7128 (9)	6687 (11)	7176 (12)
N(22)	7271 (7)	5015 (9)	7410 (8)
C(6)	7044 (9)	5729 (10)	6786 (11)
C(7)	6623 (9)	5367 (12)	5701 (11)
C(8)	6516 (9)	4420 (11)	5695 (10)
C(9)	6962 (8)	4208 (11)	6805 (10)
C(10)	7050 (9)	3331 (9)	7168 (10)
C(121)	7858 (11)	1173 (9)	7786 (12)
C(122)	8386 (15)	894 (12)	6927 (14)
C(131)	9506 (12)	1466 (11)	9954 (12)
C(132)	9069 (16)	1201 (13)	10798 (16)
C(171)	10292 (9)	4272 (9)	13021 (10)
C(172)	9596 (12)	3762 (12)	13484 (13)
C(181)	9515 (12)	6465 (9)	13292 (10)
C(182)	10474 (14)	6964 (13)	13499 (15)
C(21)	7360 (14)	8924 (10)	10415 (14)
C(22)	6404 (18)	9003 (15)	10813 (17)
C(31)	6753 (14)	8872 (10)	7960 (13)
C(32)	5545 (14)	8948 (13)	7675 (15)
C(71)	6388 (10)	5930 (9)	4725 (9)
C(72)	7318 (10)	6022 (11)	4304 (11)
C(81)	6128 (11)	3790 (9)	4725 (9)
C(82)	7001 (12)	3212 (10)	4314 (10)
C(146)	5062 (12)	5469 (14)	8445 (11)
C(141)	4332 (12)	4906 (11)	8611 (9)
C(142)	3430 (15)	5347 (15)	8758 (13)
C(143)	3250 (14)	6298 (19)	8849 (13)
C(144)	3953 (16)	6866 (12)	8696 (10)
C(145)	4867 (13)	6418 (15)	8494 (11)
C(161)	2642 (16)	412 (15)	5897 (13)
C(162)	2787 (14)	9527 (16)	6284 (15)
C(163)	2039 (23)	9208 (15)	6697 (17)
C(164)	1095 (20)	9736 (19)	6575 (17)
C(165)	955 (16)	604 (18)	6165 (20)
C(166)	1711 (17)	933 (14)	5796 (16)
C(101)	6390 (10)	2604 (8)	6495 (9)
C(102)	5556 (10)	2296 (9)	6706 (10)
C(105)	4890 (12)	1599 (11)	5911 (13)
O(105)	5104 (8)	1318 (7)	5089 (8)
O(106)	4123 (7)	1340 (6)	6217 (7)
C(106)	3455 (13)	665 (11)	5458 (13)
C(103)	5228 (10)	2635 (12)	7684 (11)
O(103)	5409 (8)	2133 (7)	8421 (8)
O(104)	4830 (7)	3487 (8)	7688 (6)
C(104)	4520 (11)	3890 (8)	8607 (11)

2424 unique reflexions were retained for use in the structure analysis. The structure was solved by Patterson and difference syntheses and refined by blocked-full-matrix least squares. All the non-hydrogen atoms were assigned anisotropic temperature factors, except for those of the 5-formyl substituent for which disorder was observed. The 26 H atoms (from a total of 60) of C(101), the secondary CH_2 groups and the C(141) phenyl ring (that situated above the porphyrin macrocycle) were included in the final cycles at geometrically calculated positions together with two group isotropic temperature factors, which refined to 0·119 (23) and 0·201 (38) Å^2 respectively. Electron density peaks corresponding to a disordered formyl group were observed for substituents at C(5), C(15) and C(20). The best description of this disorder was obtained by assigning the formyl-group C and O atoms at C(5) a site-occupation factor of 0·5 and at the other methine bridges factors of 0·25. The terminal value of $R_G[=(\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}]$ was 0·094, with $R_w[=(\Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_o|)]$ 0·078 and R 0·079.* The weights were given by $w=k[\sigma^2(F_o)+gF_o^2]^{-1}$, where k and g refined to 1·8922 and 0·002381 respectively. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). Positional parameters are in Tables 1 and 2.

Discussion. Porphyrins with eight β-pyrrolic and one or more methine bridge substituents have been termed 'highly substituted' (Fuhrhop, Witte & Sheldrick,

Table 2. *Positional parameters* ($\times 10^4$) *and isotropic temperature factors* (Å^2 $\times 10^3$) *for the disordered formyl substituent*

	x	y	z	U
C(51)	6978 (21)	7429 (18)	6408 (20)	82 (9)
O(51)	7756 (16)	7704 (14)	6235 (16)	112 (7)
C(151)	9919 (45)	2874 (37)	11358 (43)	113 (22)
O(151)	9478 (44)	2376 (41)	11806 (48)	194 (24)
C(201)	8442 (40)	7758 (28)	11814 (33)	80 (17)
O(201)	7671 (39)	7607 (35)	12104 (41)	160 (19)

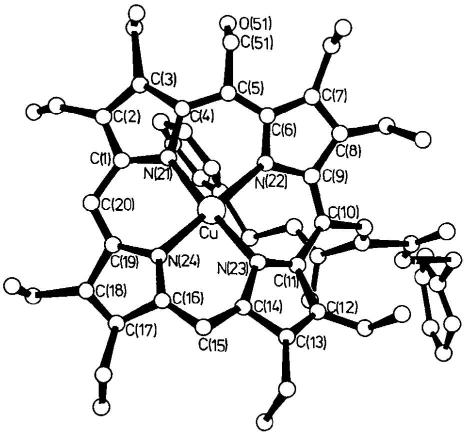

Fig. 1. A molecule of (I) in perspective.

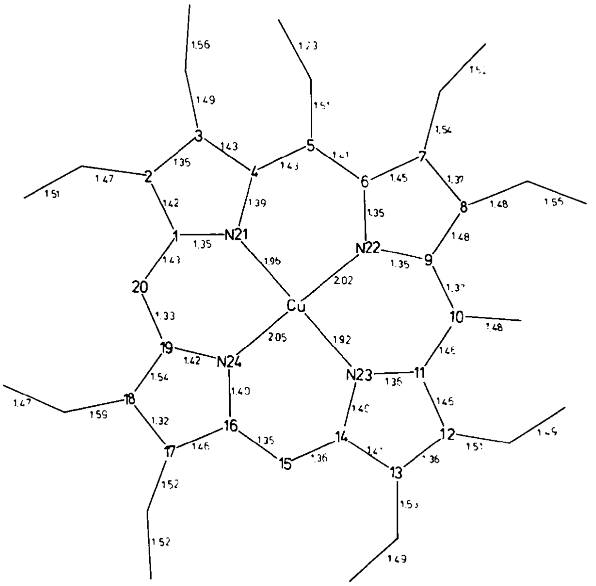

Fig. 2. Bond lengths (Å) in (I). Standard deviations are 0·01 for the C—N, 0·02 for the porphyrin macrocycle and 0·03 Å for the side-chain bonds.

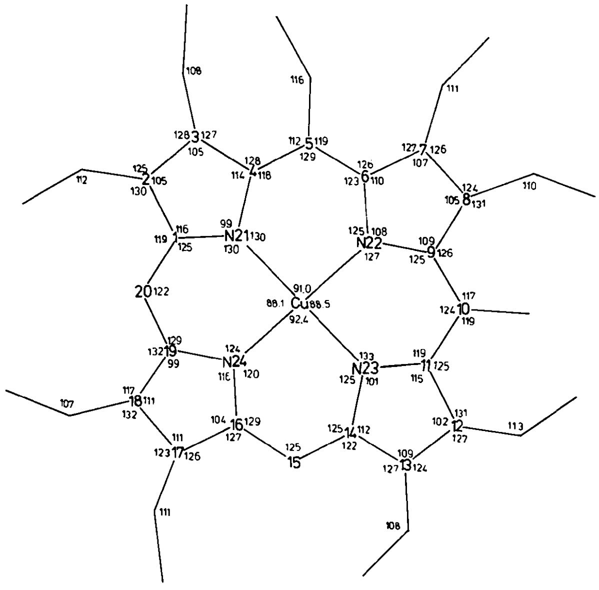

Fig. 3. Bond angles (°) in (I). Standard deviations are 0·5 for the N—Cu—N, 1 for the porphyrin macrocycle and 1–2° for the side-chain angles.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33091 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

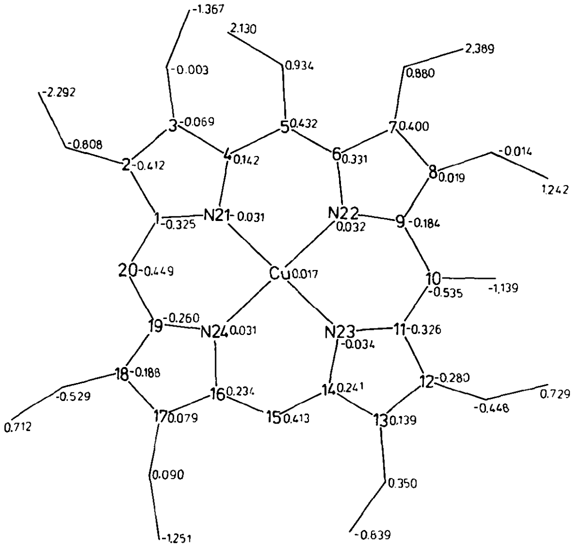

Fig. 4. Distances (Å) from the N atom least-squares plane.

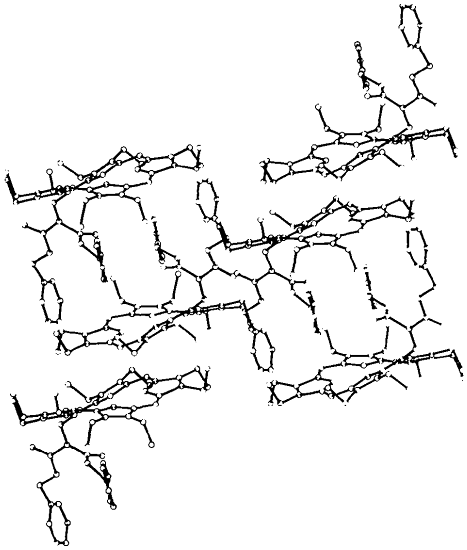

Fig. 5. Projection of the crystal structure perpendicular to |100|.

1976). The X-ray analyses of two such porphyrins, namely the title compound (I) (Fig. 1) and 2,3,7,8,12,13,17,18-octaethyl-5-[2,2-bis(ethoxycarbonyl)vinyl]-22*H*,24*H*-porphine (Sheldrick, 1977), which were briefly discussed in the same article, have demonstrated that the porphyrin macrocycle is much more flexible than was previously supposed. The structure of (I) is reported here in detail. Bond lengths and angles are given in Figs. 2 and 3.

The methine bridge C atoms in (I) are placed alternately above and below the N least-squares plane (Fig. 4) at distances in the range 0·41–0·54 Å. Large deviations are observed for the α- and β-pyrrolic C atoms in the rings neighbouring the substituted methine bridges (*A*, *B* and *C*). The fact that the aromatic character of the macrocycle is retained in (I) despite these very considerable distortions suggests that the porphyrin ring is intrinsically flexible enough to accommodate bulky substituents at the methine bridges and the β-pyrrolic positions. The Cu—N distances show very significant differences [1·92–2·05 (1) Å]. The distribution of these bond lengths and those within the macrocycle is in accordance with approximate C_2 symmetry. The phenyl ring of the *Z*-configurated ester group of the C(10) substituent is sited above and approximately perpendicular to the near-planar ligand field at the central Cu^{2+} ion. These phenyl rings from adjacent molecules are arranged parallel to one another in the crystal (Fig. 5) at a van der Waals distance, as are adjacent porphyrin systems.

Calculations were carried out with *SHELX* 76 (G. M. Sheldrick). I am indebted to Dr L. Witte for crystals and to Frau A. Borkenstein for technical assistance.

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