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[5,10,15,20-*meso*-Tetrakis(2-thienyl)porphyrinato-κ^4N]copper(II)

Yael Diskin-Posner, Srinivasan Balasubramanian, Goutam Kumar Patra and Israel Goldberg*

School of Chemistry, Sackler Faculty of Exact Sciences, Tel-Aviv University, Ramat-Aviv, 69978 Tel-Aviv, Israel

Correspondence e-mail:
goldberg@chemsg7.tau.ac.il

Key indicators

Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.046
wR factor = 0.130
Data-to-parameter ratio = 11.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, [Cu($C_{36}H_{20}N_4S_4$)], was synthesized and its molecular structure was precisely characterized by low-temperature single-crystal analysis. The molecules are located on crystallographic centers of inversion.

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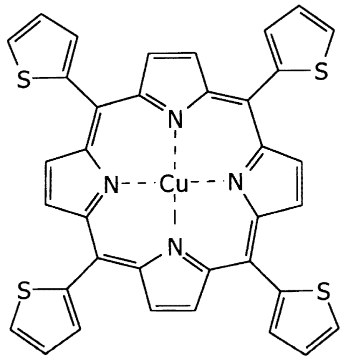
Comment

The title compound, (I), was synthesized as a potential building block for the supramolecular synthesis of multi-porphyrin arrays. The S-atom sites of the thiophene rings are potential ligating sites for coordination of Cu^I and Ag^I ions, and may thus facilitate formation of coordination polymers through external metal ion auxiliaries.



(I)

The porphyrin core is nearly planar with only a slight puckering, the deviation of the individual atoms from its mean plane not exceeding 0.01 Å. One of the thiophene rings (C18 through S22) exhibits a twofold disorder, with equally populated orientations. The latter are characterized by 50% occupancy of positions 19 and 22 by either C or S atoms, with the appropriate adjustment of the corresponding bond lengths that involve these atoms. Assumption of a single orientation (with only S19 and C22, or alternatively with only C19 and S22) raises the *R* factor for the observed reflections above 0.098 (as opposed to 0.046 for the disordered model), with a high peak near the chosen C-atom site and a deep trough near the chosen S-atom site. The dihedral angles between the ordered C13–C17 thiophene ring and the C18–S22 thiophene ring in its two equally populated orientations are 7.2 (1) and 4.6 (1)°. As opposed to related tetraaryl metalloporphyrins, which tend to crystallize as clathrates, the present compound crystallized as a pure homogeneous solid. The disorder of the

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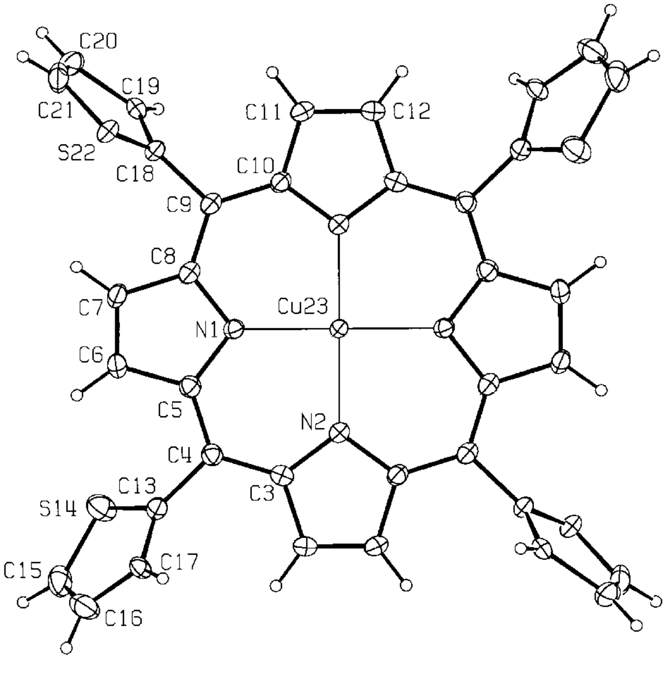

Figure 1
The molecular structure of (I). The ellipsoids represent the displacement parameters at the 50% probability level at 110 K. Only one orientation of the twofold disordered C18–S22 thiophene ring is shown. The N1—Cu23 and N2—Cu23 bond lengths are 1.999 (4) and 2.012 (4) Å, respectively.

C18–S22 ring is probably affected by the tendency to optimize intermolecular S···S cohesive interactions. In the observed structure, S14···S19($1 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$) is 3.748 (2) Å, and S14···S22(x, $1 + y$, z) is 3.796 (2) Å. A similar disorder of the C13–C17 thiophene ring does not occur, as the distance between position 17 and sites S19 or S22 of neighboring species is larger than 4.8 Å.

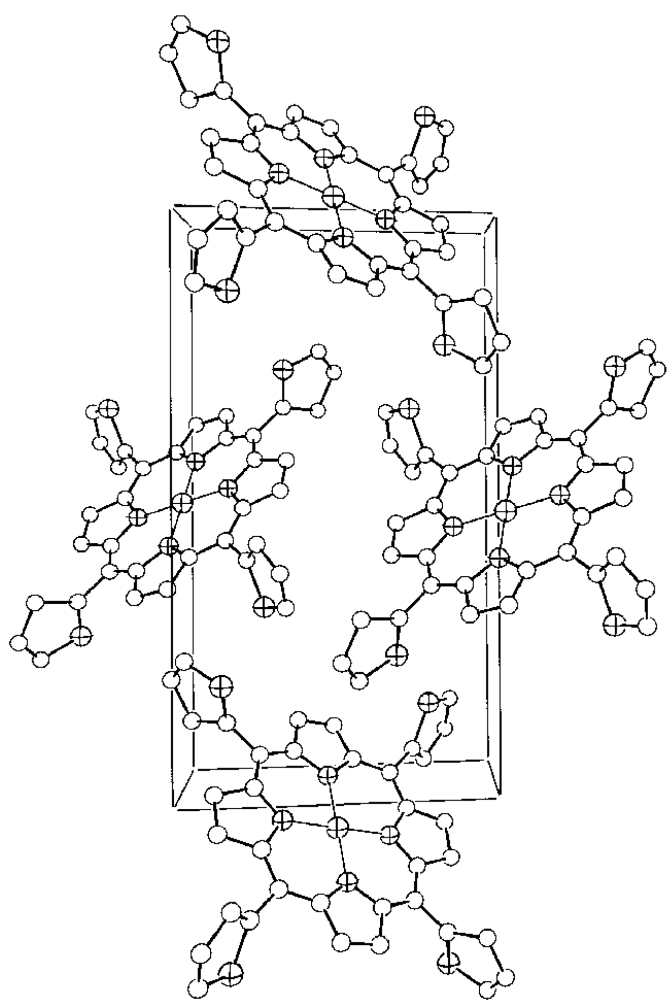

Figure 2
Crystal packing viewed down the short *a* axis of the crystal (*b* is horizontal and *c* is vertical; contents of two unit cells are shown). The mean interplanar distance between neighboring molecules displaced along the *a* axis is 3.6 Å. Atoms are shown as arbitrarily sized spheres; the Cu, N, and S atoms are denoted by crossed circles.

Experimental

Pyrrole and all common solvents were obtained from Aldrich. The thiophene-2-carbaldehyde component was prepared by mixing thiophene (21 g, 250 mmol), dimethylformamide (DMF; 23 g, 314 mmol) and dichloroethane (100 g, 1010 mmol) at 273 K. To this solution, phosphorus oxychloride (48 g, 313 mmol) was added dropwise with vigorous stirring. The resulting mixture was heated in an oil bath, neutralized with sodium acetate trihydrate (200 g), and the product was extracted with diethyl ether. The ether layer was washed several times with sodium bicarbonate and then with brine, and finally dried over anhydrous sodium sulfate. The solvents were distilled off and the crude thiophene-2-carbaldehyde was purified by reduced-pressure distillation to yield a pale-yellow viscous oil (18 g, 64%). ^{1}H NMR ($CDCl_3$): δ 7.23 (*m*, 2H), 7.79 (*m*, 3H, Ar-H), 9.95 (*s*, 1H, CHO). A mixture of pyrrole (2.71 g, 40.0 mmol) and the thiophene-2-carbaldehyde (4.48 g, 40 mmol) was added dropwise to 150 ml of boiling propionic acid. The mixture was refluxed with stirring for 1 h, cooled to room temperature and allowed to stand overnight. The resulting dark-coloured mixture was filtered, washed with methanol and then with hot water, and purified by column chromatography (silica, 63–200, 60 Å), using a mixture of petrol ether and chloroform as eluent. This procedure yielded 2.0 g (31%) of tetra(2-thiophene)porphyrin. The latter was then dissolved in DMF heated to boiling, and treated with excess of copper(II) acetate. The resulting product was purified by column chromatography (silica, 63–200, 60 Å) using a mixture of chloroform and ethyl acetate as eluent to yield (I) in high yield (90%). The product was characterized by ^{1}H NMR and MS analyses. ^{1}H NMR ($CDCl_3$): δ 7.53 (*m*, 1H, Ar-H), 7.7 (*m*, 1H, Ar-H), 7.87 (*m*, 1H, Ar-H), 9.04 (*s*, 1H, CHO).

Crystal data

$[Cu(C_{36}H_{20}N_4S_4)]$
$M_r = 700.34$
Monoclinic, $P2_1/c$
$a = 6.5550$ (2) Å
$b = 10.9180$ (3) Å
$c = 20.5590$ (6) Å
$\beta = 93.2030$ (15)°
$V = 1469.06$ (7) Å^3
$Z = 2$

$D_x = 1.583$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2307 reflections
$\theta = 2.7$–25.4°
$\mu = 1.06$ mm^{-1}
$T = 110$ (2) K
Prism, dark blue
0.35 × 0.20 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
1.0° φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{\min} = 0.707$, $T_{\max} = 0.857$
4433 measured reflections
2587 independent reflections
2307 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$
$\theta_{\max} = 25.4°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 13$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.130$
$S = 0.98$
2587 reflections
223 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 6.3287P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.118$
$\Delta\rho_{\max} = 0.88$ e Å^{-3}
$\Delta\rho_{\min} = -0.78$ e Å^{-3}

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski, 1985); data reduction: *DENZO*; program(s) used to solve structure: *DIRDIF*96 (Beurskens *et al.*, 1996); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

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