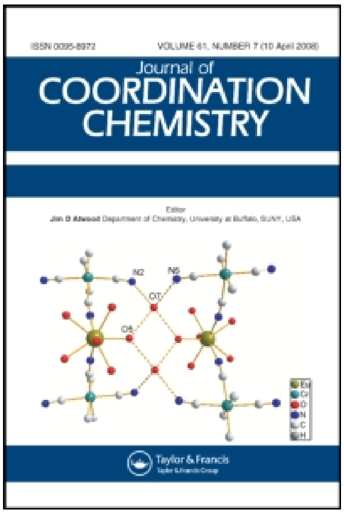

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The crystal structure of octakispentoxy-phthalocyaninatocopper with pyridines axially substituted: the molecules stacked with J-aggregates

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For coordination with two pyridines at the axis, the ring skeleton of octakispentoxyphthalocyaninatocopper maintains planar conformation, different from the structure of octakisbutoxyphthalocyaninatocopper reported previously. The structure shows all molecules stacked along the *b* axis to form a one-dimensional molecular chain; neighboring molecules in the chain are arranged as J-aggregates, consistent with its crystal diffuse reflectance spectroscopy (DRS) having a red shift compared with its electronic absorption spectroscopy in pyridine.

Keywords: Substituted phthalocyanines; Crystal structure; J-aggregates

1. Introduction

Properties of phthalocyanines, such as spectroscopic, electronic, and magnetic properties, thermo-stabilities, and catalytic activities, may be modified by introducing suitable ligands to the axial position of the center atom or by substituting some groups to the outer benzene rings [1]. The relationship between the structures and properties of modified phthalocyanines is important for exploring their applications.

In a series of work on substituted Pcs, we have determined crystal structures of alkoxy and aroxy substituted Pcs and found that the ring skeleton of substituted Pcs without axial coordination always deviated from planar conformation, attributed to the steric congestion of substituents [2]. The effect of axial ligands was not clear despite the structure of pyridine and methanol coordinated octakisbutoxyphthalocyaninatocobalt reported [3]. Here we report the crystal structure and diffuse reflectance spectroscopy of octakispentoxyphthalocyaninatocopper with two pyridines at the axes.

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2. Experimental

Reactions were performed under nitrogen. The starting material, 3,6-dipentoxyphthalonitrile, was prepared using reported procedures [4], and all other reagents were commercially available and used without further purification. Elemental analyses were obtained with Vario EL III elemental analysis instrument. Diffuse reflectance spectra and electronic absorption spectra were recorded with a PE-Lambda800 UV/Vis spectrophotometer at room temperature.

2.1. *Synthesis of title compound*

The title compound was obtained by a procedure similar to the literature [3, 4]. A mixture of 3,6-dipentoxyphthalonitrile (0.6044 g, 2.01 mmol), cuprous chloride (0.1342 g, 1.34 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1.2 mL, 8.45 mmol) in 1-pentanol (5.0 mL) was refluxed at 160°C for 10 h under a nitrogen atmosphere. As the reaction mixture was cooled to room temperature, methanol (100 mL) was added. The precipitate was filtered off and washed by methanol, then dissolved in chloroform and purified by chromatography (silica gel, chloroform as eluent). The solvent was evaporated from the green eluate and the residue recrystallized from CH_2Cl_2/CH_3OH to give dark-green micro-crystal powders, which are not coordinated in axial positions. Yield: 0.116 g (17.4%), Anal. Calcd for (%) for $C_{82}H_{106}CuN_{10}O_8$: C, 69.20; H, 7.51; N, 9.84, found: C, 69.45; H, 7.26; N, 9.68. Crystals with two pyridines for X-ray diffraction were obtained by evaporation of the solution of the product in pyridine.

2.2. *Determination of crystal structure*

Reflection data were collected from a single crystal ($0.75 \times 0.66 \times 0.38\,\mathrm{mm}^3$) on a Rigaku RAXIS-RAPID (an X-ray imaging plate system) by using graphite-monochromated Mo-Kα ($\lambda = 0.710688\,\text{Å}$) radiation. The cell parameters were determined from 6153 reflections. The ranges for data collection are as follows: $\theta = 1.95$–$27.48°$, $h = -12$–12, $k = 0$–14, $l = -25$–24. A total of 9849 reflections were collected, and 6823 were unique with $R_{\mathrm{int}} = 0.0471$, of which 3804 were considered to be observed with $I \geq 2\sigma(I)$. The data were corrected for *LP* factors without absorption correction ($\mu = 0.332\,\mathrm{mm}^{-1}$). The structure was solved by direct methods (SHELXS-97, Sheldrick, 1990) and refined using full-matrix least-squares techniques on F^2 (SHELXL-97, Sheldrick, 1997) [5]. The non-hydrogen atoms were refined anisotropically whereas the hydrogen atoms were placed on calculated positions and refined with isotropic thermal parameters. For disorder of the substituents, refinements were performed by fixing the C–C (1.5 Å) distances of some substituent chains but not do statistical disposal on them. The axial pyridine groups were also performed with rigid fixing. The final results were obtained with $R = 0.0758$ for 3804 observed reflections ($I \geq 2\sigma(I)$); $R = 0.1322$ and $wR = 0.2023$ for all 6823 unique reflections used ($w = 1/[\sigma^2(F^2) + (0.1000P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$). The program used to prepare the drawings is ORTEX (P. McArdle, 1995) and that for data output is SHELXS-97/2 (Sheldrick, 1997).

3. Results and discussion

3.1. *Synthesis*

As reported previously [2, 3], the title compound can be obtained only in presence of DBU as catalyst in alcohol solvents because of the intra-molecular steric congestion of bulky substituents.

Usually, structures of substituted phthalocyaninatocopper (CuPcs) obtained from mixed solvents (CH_2Cl_2/C_2H_5OH) were four-coordinate [2b, 2d]. In order to find out whether the CuPcs can form six-coordinate complex, we tried to grow crystal from strongly coordinating pyridine solvent and finally got the title single crystal with two pyridines on the axes.

3.2. *Structure description*

The crystal system of the title compound is triclinic, space group $P\bar{1}$ with $a = 9.8780(12)$ Å, $b = 10.882(2)$ Å, $c = 19.4960(12)$ Å, $\alpha = 105.940(3)°$, $\beta = 99.978(4)°$, $\gamma = 950522(9)°$, $C_{82}H_{106}CuN_{10}O_8$, $Mr = 1423.31$, $Z = 1$, $V = 1961.5(5)$ Å^3, $D_c = 1.205\ \mathrm{g\,cm^{-3}}$, $F(000) = 761$, μ(Mo-Kα) $= 0.339\ \mathrm{mm^{-1}}$.

The molecular structure is shown in figure 1, and selected bond lengths and angles are listed in table 1. The ring skeleton of the title compound maintains planar conformation where C4 has the largest distance of 0.129 Å from the mean plane of the ring system and the stretch directions of substituents somewhat deviate from the ring plane, which is different from the saddle shape of octakisbutoxy-phthalocyaninatocopper reported previously [2d]. Two pyridine groups coordinated axially to the Cu with distances between the N of pyridines and the Cu are 2.677 and 2.605 Å, longer than the distances

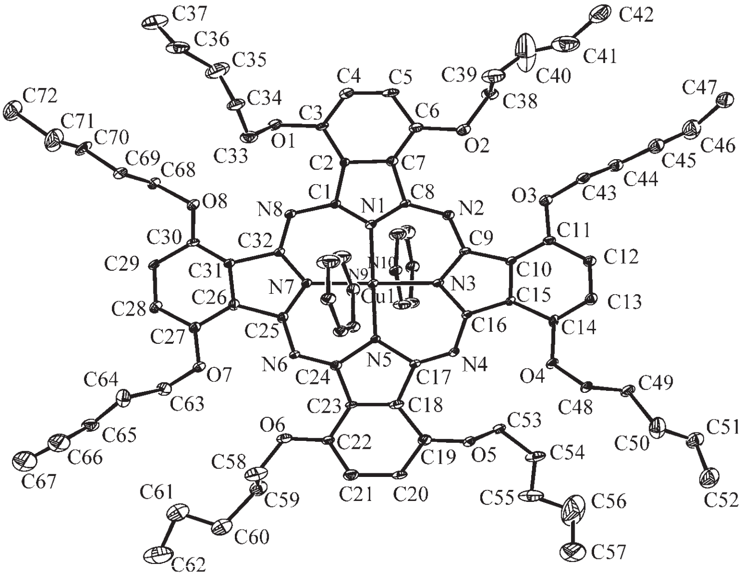

Figure 1. The Molecular structure of the title compound with atom numbering scheme. Thermal ellipsoids are shown at the 20% probability level with axial pyridine groups not labeled atoms for clarity.

Table 1. Selected bond lengths (Å) and bond angles (°).

Cu(1)–N(1)	2.027(12)	Cu(1)–N(3)	1.959(12)
Cu(1)–N(5)	1.906(10)	Cu(1)–N(7)	1.985(11)
N(1)–C(1)	1.272(17)	C(1)–C(2)	1.461(16)
C(2)–C(3)	1.393(16)	C(3)–C(4)	1.34(2)
C(4)–C(5)	1.31(3)	C(5)–C(6)	1.41(2)
C(6)–C(7)	1.35(2)	C(7)–C(8)	1.50(2)
C(2)–C(7)	1.415(18)	N(8)–C(1)	1.400(16)
N(2)–C(8)	1.338(17)	O(1)–C(3)	1.426(17)
Cu(1)–N(9)	2.677(83)	Cu(1)–N(10)	2.605(24)
C(1)–N(1)–Cu(1)	124.1(8)	N(1)–Cu(1)–N(7)	88.9(4)
N(1)–C(8)–C(7)	109.6(12)	C(8)–N(1)–C(1)	111.8(12)
N(1)–C(1)–C(2)	111.8(9)	C(3)–C(2)–C(1)	139.4(11)
C(5)–C(4)–C(3)	123.6(15)	C(4)–C(5)–C(6)	121.8(17)
C(7)–C(2)–C(3)	117.2(12)	C(7)–C(6)–C(5)	115.1(18)
C(6)–C(7)–C(8)	132.6(15)	N(9)–Cu(1)–N(10)	174.7(74)

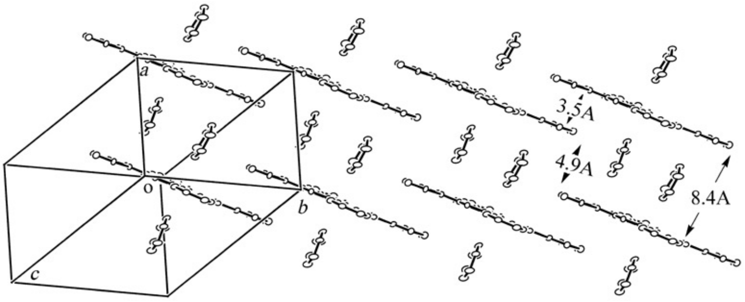

Figure 2. The packing of molecules in *ab* plane with pentyloxy groups omitted for clarity.

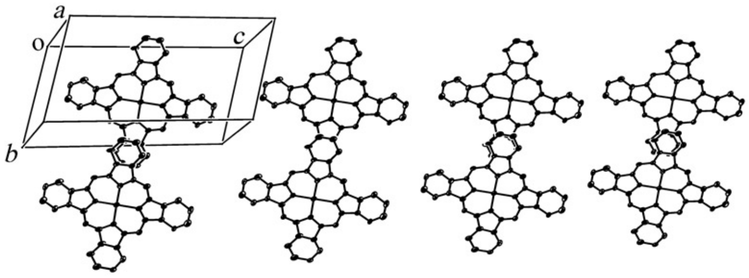

Figure 3. The packing of molecules in *bc* plane with pentyloxy and pyridine groups omitted for clarity.

between N of isoindole and Cu (2.027 and 1.959 Å). The planes of pyridine are basically perpendicular to that of Pc ring, and the angle between the two pyridine planes is 174.7°.

The molecule packing pattern in the planes *ab* and *bc* are shown in figures 2 and 3. We can see that along the *b* axis the Pc rings are parallel to each other to form a one-dimensional chain. In the molecular chain, the neighboring two Pc rings are arranged as J-aggregates by benzene rings of isoindoles, namely, a benzene ring (C12–C13) of one molecule and a benzene ring (C28–C29) of another adjacent molecule with a distance of 3.5 nm, which is close to the van der Waals distance of a planar aromatic system [6].

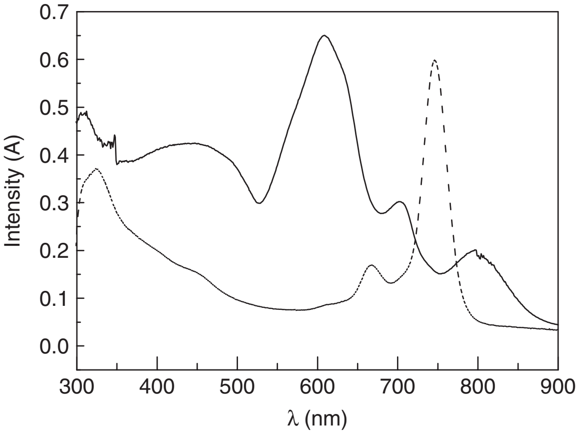

Figure 4. The crystal DRS of the title compound (solid line) and its UV-Vis absorption spectroscopy in pyridine (dot line).

Along the *a* axis, the one-dimensional chains are separated by nearly parallel pyridine rings with a closest vertical distance of 4.9 Å. Along the *c* axis, parallel one-dimensional molecular chains are substituents not overlapped.

According to Cook [7], introductions of the bulky subtituents always lead to distortions of the Pc skeleton, mainly attributed to the intramolecular steric congestion. In our studies [2d], when neighboring Pc molecules are aggregate (the distances are close to 3.5 Å), slip overlap brought by their intramolecular steric congestion also distorts the Pc. In this article, vertical distances between the closest CuPcs are 3.5 Å with a smaller overlap because of the axial pyridine coordination. As a result, the Pc ring keeps planar conformation. So the appropriate overlap of neighboring Pc molecules is important for the distortions of their skeleton. Full or small overlap leads to the planar skeleton.

3.3. *Spectroscopic properties*

Figure 4 shows the diffuse reflectance spectroscopy (DRS) of the title compound's crystal, where the peaks are blue and red shifted compared with its electronic absorption spectroscopy in pyridine ($\lambda = 741$ nm). According to Kasha [8], the different aggregate modes of aromatic compounds always lead to different electronic absorption spectra of their aggregates. When dimers are assembled face to face, their spectra are blue shifted compared to monomer. When they assemble end to end (J-aggregates) their spectra red shift. In this article, the molecules stacked face to face are much closer in the crystal than in the solvent, which leads to its DRS blue shift. The closest two Pc molecules stack like J-aggregates in its crystal bring on the DRS red shift. As a result, the DRS of the title crystal show three peaks at 609, 703 and 797 nm.

4. Conclusion

In summary, the structure of the phthalocyaninatocopper with eight pentoxy substitutents and two pyridines is described. The skeleton of its Pc ring keeps the planar conformation, attributed to the small overlap of the closest two molecules which is blocked by the axial pyridines. The small overlaps also lead to the molecules stacked like J-aggregates, confirmed by DRS.

Supplementary data

CCDC 286260 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk).

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