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Synthesis, crystal structure and characterization of a new zinc phthalocyanine complex

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Abstract

A new complex [ZnPc(H₂O)]·2DMF (1), where Pc = phthalocyanine and DMF = *N*,*N*-dimethylformamide, has been synthesized and its crystal has been determined by single-crystal X-ray diffraction method. The compound crystallizes in the triclinic space group *P* - 1. The lattice parameters are a = 11.668(5) Å, b = 12.186(5) Å, c = 13.939(6) Å, $\alpha = 78.697(7)^{\circ}$, $\beta = 88.045$ (7)°, $\gamma = 62.949(7)^{\circ}$, V = 1727.4(12) Å³ and Z = 2. The Zn(II) ion is five-coordinated by four nitrogen atoms from Pc ligands and one oxygen atom from one water molecule. Notably, there are strong π - π interactions between Pc ligands, leading to 1D superamolecular structure. Moreover, the elemental analyses, FT-IR, UV-vis and Fluorescence spectra for this complex were also determined. © 2006 Elsevier B.V. All rights reserved.

Keywords: ZnPc; Crystal structure; FT-IR; UV-vis; Fluorescence

1. Introduction

Since the firstly reported paper by Braun and Tcherniac about phthalocyanine, there has been extensive interest in phthalocyanine and its derivatives, and the search for new phthalocyanines is one of the fundamental studies [1]. It is well known that the phthalocyanines are P-type semiconductor characterised by high thermal and chemical stability. They also exhibit interesting optical, electrical, magnetic and catalytic properties, and are widely applied to many fields such as dyes [2], chemical sensors [3], electrochromism [4], batteries [5] and photodynamic therapy (PDT) [6].

On the other hand, the metal complexes containing phthalocyanine were the field of many studies and particularly over the recent years. Among phthalocyanine complexes the ZnPc derivatives are particularly interesting owing to their unique photosensitizing properties for PDT [7–9], magnetic circularly polarized luminescence (MCPL), absorption and magnetic circular dichroism (MCD) spectra. Thus, the syntheses of new ZnPc and its derivative materials are of intensive importance. In this paper a new compound $[ZnPc(H_2O)]$ ·2DMF (1) was presented, and the FT-IR, UV-vis and fluorescence spectra were also applied to characterize this complex.

2. Experiment

2.1. Preparation

Traditionally, metal phthalocyanine complexes were prepared in the high-boiling solvents such as 1-chloronaphthalene, nitrobenzene, and 1,2-dichlorobenzene. However, the [ZnPc(H₂O)]·2DMF (1) was directly synthesized in our laboratory through anhydride method [10]. A mixture of phthalic anhydride, zinc dichloride, urea and ammonium molybdate was stirred for about 1 h at room temperature, sealed in a 23-ml Teflon-lined stainless steel autoclave and heated at 200 °C for 3 days under autogenous pressure. After washed with diluted HCl solution, the product was placed in a Soxhlet extractor and extracted for 24 h. The dark green single crystals of [ZnPc(H₂O)]·2DMF (1) suit-

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able for X-ray analysis were obtained by slow evaporation of air-exposed DMF solution at room temperature, and the same complex [ZnPc(H₂O)]·2DMF is also obtained after the complex is re-crystallized from DMF. At the same time many other methods are applied to crystallize commercial zinc phthalocyanine (ZnPc) from DMF containing small amount of water, but no compound (powder or crystal) was in agreement with our title compound. So the ZnPc(H₂O) framework may be formed in the process of synthesis before ZnPc(H₂O) was dissolved in DMF. Calc. for C₃₈H₃₂N₁₀O₃Zn: C, 61.50; H, 4.35; N, 18.87%. Found: C, 61.70; H, 4.42; N, 18.65%.

2.2. X-ray data collection

Crystallographic data of compound 1 were collected on a Bruker-Apex Smart CCD diffractometer equipped with a normal-focus, 2.4 kW X-ray source (graphite-monochromated Mo–K α radiation with $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA with increasing ω (width of 0.3° and exposure time 30 s per frame). All the structures were solved by direct methods using the program SHELXS-97 and refined by full-matrix least-squares techniques against F^2 using the SHELXTL-97 crystallographic software package [11]. All non-hydrogen atoms were easily found from the difference Fourier map and refined anisotropically, whereas the hydrogen atoms of the organic molecules were placed by geometrical considerations and were added to the structure factor calculation. The detailed crystallographic data and structure refinement parameters for 1 are summarized in Table 1.

2.3. Physical measurements

The FT-IR spectra were recorded in the range $400-4000 \text{ cm}^{-1}$ on an Alpha Centaurt FT-IR spectrophotome-

Table 1

Crystallographic data and final refinement parameters for $[ZnPc(H_2O)]\mbox{-}2DMF\ (1)$

Chemical formula	$C_{32}H_{18}N_8OZn$	
Molecular weight	742.11	
Temperature (K)	293(2)	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
a (Å)	11.668(5) Å	
b (Å)	12.186(5) Å	
$c(\mathbf{A})$	13.939(6) Å	
α (°)	78.697(7)	
β (°)	88.045(7)	
γ (°)	62.949(7)	
$V(\text{\AA})^3$	1727.4(12)	
Z	2	
<i>F</i> (000)	768	
D_{calc} (g cm ⁻³)	1.427	
Reflections collected	10,829	
Reflections observed	7661	
$R\left[I > 2\sigma(I)\right]$	0.0514	
$wR[I > 2\sigma(I)]$	0.0871	
Goodness-of-fit	0.924	

ter using KBr pellets. The UV–visible spectra (200– 1000 nm) were measured in DMF solution on a Varian Cary 500 UV-Vis-NIR scan spectrophotometer. The fluorescence spectrum was determined on a Cary Eclipse fluorometer. Elemental analyses for C, H and N were performed on a Perkin-Elmer 2400 CHN elemental analyzer.

3. Results and discussion

3.1. Crystal structure of $[ZnPc(H_2O)]$ ·2DMF (1)

Selected bond distances and angles are given in Table 2. The structure of $[ZnPc(H_2O)]$ 2DMF (1) is shown in Fig. 1. The compound (1) consists of one ZnPc, one water molecule and two DMF molecules. The central Zn(II) ion is five-coordinated by four nitrogen atoms from Pc ligand and one oxygen atom from water molecule. The Zn(II) atom orbitals in this coordination environment assume the sp^2d^2 hybridisation. The Zn-N distances range from 2.024(2) to 2.014(2) Å, and the axial Zn–O (OW1) bond distance is 2.077(2) Å which is much shorter than that in $ZnPc(H_2O)$ complex (the Zn–O bond distance is 2.20 Å) [12]. In compound (1) the C-N bonds are typical conjugated π -electron systems and their distances are similar to those observed in other phthalocyanine structures [13-15]. Notably, the Zn(II) atom is at an inversion center, and the distance between the Zn(II) atom and the leastsquare plane defined by N1-N4 toward the water molecule is about 0.38 Å.

The water molecule and the DMF molecules are all potential hydrogen-bonding sites. The hydrogen-bonding interactions occur between OW1 and two DMF molecules, where the OW1 water molecule acts as the hydrogen donor, whereas the DMF molecules only play a role of hydrogen acceptors. The distances of OW1···O1 and OW1···O2^{#1} (^{#1}1 - x, 1 - y, 1 - z) are 2.722(3) Å and 2.687(3) Å, respectively. The angles of OW1···HW12···O1 and OW1···HW11··O2^{#1} are 175(3)° and 166(4)°, respectively. These hydrogen-bonded data are in good agreement with those in the reported compounds [16].

In Fig. 2, the compound (1) is stacked in a herringbone fashion along crystallographic *b* axis. As one of important types of supramolecular forces, $\pi \cdots \pi$ stacking shows a specific structural requirement for substrate recognition or the arrangement of complicated architectures. In complex (1), strong intermolecular $\pi \cdots \pi$ stacking is present. One is formed between two Pc ligands (labeled α , centroid-to-centroid distances: 3.48 Å) and the other between two Pc ligands (labeled β , centroid-to-centroid distances: 3.62 Å). The α -type $\pi \cdots \pi$ interactions link the (1) to form dimer, which is further connected through the β -type $\pi \cdots \pi$ interactions, resulting in an infinite 1D superamolecular chain (Scheme 1 and Fig. 3).

The average distances and angles of various Zn(II) porphyrin derivatives including ZnPcCl [17], $ZnTPP(H_2O)$ (TPP = tetraphenylporphine) [18], (*n*-hexyl)ZnPc [19] and

Table 2 Selected bond length (Å) and angles (°) for $[Z_nP_C(H_iO)]^2DME(1)$

beleeted bond length (11) and angles (1) for [2111 0(1120)]21	
Bond lengths Zn(1)-N(1) Zn(1)-N(3)	2.024(2) 2.014(2)
N(1)C(1) N(2)C(9) N(3)C(24)	1.363(3) 1.366(4) 1.364(4)
N(4)C(25) N(5)C(8) N(6)C(16)	1.363(3) 1.330(3) 1.343(4)
N(7)-C(24) N(8)-C(1) C(2)-C(1) C(10)-C(9) C(18)-C(17) C(26)-C(25) C(2)-C(7) C(18)-C(23)	1.336(3) 1.329(4) 1.469(4) 1.463(4) 1.457(4) 1.449(4) 1.385(4) 1.393(4)
Zn(1)—OW(1) Zn(1)—N(2) Zn(1)—N(4)	2.077(2) 2.018(2) 2.020(2)
N(1)C(8) N(2)C(16) N(3)C(17)	1.367(4) 1.369(3) 1.367(3)
N(4)C(32) N(5)C(9) N(6)C(17)	1.365(3) 1.335(3) 1.335(3)
$\begin{array}{l} N(7)-C(25) \\ N(8)-C(32) \\ C(7)-C(8) \\ C(15)-C(16) \\ C(23)-C(24) \\ C(31)-C(32) \\ C(10)-C(15) \\ C(26)-C(31) \end{array}$	1.339(3) 1.337(3) 1.470(4) 1.452(4) 1.459(4) 1.458(4) 1.401(4) 1.399(4)
Bond angles N(2)-Zn(1)-N(1) N(3)-Zn(1)-N(2) N(4)-Zn(1)-N(1) N(1)-Zn(1)-OW(1) N(3)-Zn(1)-OW(1) C(1)-N(1)-C(8)	87.94(10) 88.20(10) 87.84(9) 101.66(9) 98.90(9) 109.5(2)
C(24)-N(3)-C(17) $C(8)-N(5)-C(9)$ $C(24)-N(7)-C(25)$ $N(3)-Zn(1)-N(1)$ $N(3)-Zn(1)-N(4)$ $N(4)-Zn(1)-N(2)$	108.6(2) 123.4(3) 123.3(3) 159.42(9) 88.03(9) 157.50(9)
N(2)-Zn(1)-OW(1) N(4)-Zn(1)-OW(1) C(9)-N(2)-C(16) C(25)-N(4)-C(32) C(17)-N(6)-C(16) C(1)-N(8)-C(32)	98.24(10) 104.26(10) 108.8(2) 108.8(2) 123.6(2) 123.6(2)

ZnPc(H₂O), and ZnPc [20] are shown in Table 3. Ct is the center of the square formed by the four central nitrogen atoms. C_{α} and C_{β} represent α - and β -carbon atoms of a pyrrole unit, respectively. N_p and N_b represent a pyrrole nitrogen atom and an azamethine atom, respectively. The comparable values observed for ZnPcCl, ZnTPP(H₂O)



Fig. 1. ORTEP view of [ZnPc(H₂O)]²DMF (1).

and (n-hexyl)ZnPc are 2.35, 2.20 and 2.17 Å, respectively. It is can be seen that the Zn-O (water) bond distance (2.077 Å) for our compound [ZnPc(H₂O)]·2DMF (1) is the shortest among others. The Zn-N_p distance of 2.019(2) Å for $[ZnPc(H_2O)]$ 2DMF (1) is very close to that of ZnPc(1.980 Å), and shorter than those of other three complexes. This indicates that Zn(II) atom in compound ZnPc is almost coplanar in the absence of axial ligand. In contrast to the N_p - C_α values of ZnPc, ZnPcCl and (*n*-hexyl)ZnPc the corresponding values of [ZnPc(H₂O)]²DMF (1) are obviously nearer to that of ZnPc, and somewhat different from those of ZnPcCl and (n-hexyl)ZnPc. In the same manner considering the value of C_{α} -N_b, C_{α} -C_{β} and C_{β} — C_{β} , respectively, the same consequence can be obtained. Thus it also indicates that the axial water molecule has less influence on Pc ring than the axial ligand Cl^{-} ion and *n*-hexyl group.

3.2. Characterization

In the IR spectrum, the compound (1) has absorption at 888, 1062, 1286 cm⁻¹ as well as in the 1410–1486 cm⁻¹ region, corresponding to the presence of ZnPc (Fig. 4) [21]. The IR spectrum also showed strong bands at 3432 and 3051 cm⁻¹ that can be attributed to the O—H stretching of the water and C—H stretching mode for the phenyl ring, respectively [12]. The strong peak at 1456 cm⁻¹ is assigned to $v_{\rm s}$ (—CN—C=C—) groups. The two peaks at 776 and 727 cm⁻¹ are attributed to the C—H vibrations [22]. These features could be completely confirmed by the single crystal X-ray diffraction study.

The UV-visible spectrum in DMF indicates the Soret band at 331 nm and Q band at 669 nm, which are the typical bands characteristic of ZnPc (Fig. 5a). In contrast with the corresponding bands of ZnPc (340 and 670 nm) (Fig. 5b), a slight blue shift occurs in our compound (1) [23]. The blue shift of the 340–331 nm most probably



Fig. 2. The crystal structure viewed along the b axis.



Scheme 1. Schematic representation of the $\pi \cdots \pi$ interactions between the Pc ligands of compound (1).



Fig. 3. The packing structure of compound (1).

resulted from the remaining water molecule because the water molecules usually show stronger coordination ability than the DMF molecules for Zn(II) ions and the interaction between the Zn(II) ion and the coordinating water molecule slightly affects the electron distribution of ZnPc. The Soret band corresponds to the excitation between the $la_{2u}(\pi)$ and the $le_g(\pi^*)$ states. The Q-band is associated

with the excitation between the HOMO- A_{1g} ground state $(a_{1u}^2(\pi))$ and the degenerate LUMO – $(e_g(\pi^*))$ -the first excited singlet state, which has E_u symmetry from the $(a_{1u}^1e_g^1)$ configuration [24].

The emission spectra of compound (1) in DMF with different concentrations 5.0×10^{-4} M, 3.0×10^{-4} M, 2.0×10^{-4} M, 1.5×10^{-4} M and 1×10^{-4} M were recorded at

Table 3 The average lengths (\AA) and angles (°) of characteristic bonds in ZnPc derivatives

	ZnPc	ZnPcCl	(H ₂ O)ZnTPP	(n-Hexyl)ZnPc	[ZnPc(H ₂ O)]·2DMF
Ct-M	0	0.59	0.19	0.48	0.38
Ct-N _p		1.95	2.04	2.00	1.98
M-N _p	1.980	2.034	2.05	2.06	2.019(2)
M—L		2.35	2.20	2.17	2.077(2)
$N_p - C_{\alpha}$	1.369(3)	1.380(8)	1.38	1.38	1.366(3)
$C_{\alpha} - N_{b}$	1.333(3)	1.332(9)	1.42	1.34	1.336(3)
$C_{\alpha} - C_{\beta}$	1.455(3)	1.474(9)	1.43	1.47	1.452(4)
$C_{\beta} - C_{\beta}$	1.400(3)	1.422(10)	1.37	1.43	1.409(4)
$\angle C_{\alpha} N_{p} C_{\alpha}$			105.4	109.3	108.9(2)
$\angle N_b$			125.9	124.5	123.5(2)
Ligand		Cl	0	Ν	0



Fig. 4. FT-IR spectrum for compound (1).



Fig. 5. Uv–vis absorption spectra for compound (1) (a) and ZnPc (b) in DMF.

room temperature after corrected for self-absorption, respectively. As shown in Fig. 6, the compound (1) exhibits two strong emission peaks that were about at 699 nm and



Fig. 6. Emission spectra ($\lambda_{ex} = 550 \text{ nm}$) for compound (1) in DMF. The concentrations of compound (1) are $5.0 \times 10^{-4} \text{ M}$, $3.0 \times 10^{-4} \text{ M}$, $2.0 \times 10^{-4} \text{ M}$, $1.5 \times 10^{-4} \text{ M}$ and $1 \times 10^{-4} \text{ M}$ from (1) to (5), respectively.

at 743 nm ($\lambda_{ex} = 550$ nm). Contrast to the emission wavelength (678 and 745 nm) of compound ZnPc, the bathochromic shift (21 nm) and the corresponding blue shift (2 nm) may be attributed to the presence of coordinated water molecules for the compound (1) [23,25,26].

4. Conclusion

A new complex $[ZnPc(H_2O)]$ ·2DMF (1) has been rationally synthesized through anhydride method. The Zn(II) ion is five-coordinated by four nitrogen atoms from Pc ligands and one oxygen atom from one water molecule. The strong π - π interactions between Pc ligands result in 1D superamolecular structure. The FT-IR, UV-vis and fluorescence spectra results are in good agreement with the crystal structure. The systemic studies on related ZnPc compounds are under way in our laboratory.

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Appendix A. Supplementary data

Additional material consisting of atomic coordinates, anisotropic thermal parameters, a full list of bond lengths and angles for the ZnPc(H₂O) complex have been deposited with Cambridge Crystallographic Data Centre in CIF format as supplementary publications No. CCDC 287273. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2006.05.030.

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