Notes

Synthesis, Characterization and Crystal Structure of (α-Aminopyridine-*N*)-(5,10,15,20-tetraphenylporphyrinato) Cadmium(II) Acetone Solvate

Pu Su Zhao,[†] Fang Fang Jian,[*] and Lan Zhang

[†]Jiangsu Key Laboratory for Chemistry of Low-Dimensional Materials, Huaiyin Teachers College,
Huaian, Jiangsu, 223300, P. R. China
New Materials & Function Coordination Chemistry Laboratory, Qingdao University of Science and Technology,
Qingdao Shandong, 266042, P. R. China. [*]E-mail: zhaopusu@163.com

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Metalloporphyrins have been extensively studied due to their roles in many biological processes, such as oxygen carriers in haemoglobin and myoglobin[1-3] and as enzyme model systems. The reactivity of synthetic metalloporphyrins with various axial liagnds has also been intensively studied for a few years, since it has been recently shown that anionic ligands of iron (III) porphyrin as well as manganese (III) porphyrin complexes play an important role in the catalytic oxygenation of hydrocarbons.[4,5] On the other hand, the Cd(II) ion is an important transition metal element and many cadmium(II) porphrin complexes have been studied.[6-8] However, till now, to the best of our knowledge, the Cd(II) porphhrin complexes having axial ligands are little. Recently, in our laboratory, the title complex of (α-aminopyridine-*N*)-(5,10,15,20-tetraphenylporphyrinato) cadmium(II) acetone solvate, in which α-aminopyridine is used as an axial ligand, has been synthesized. Natural population analysis on the title complex also has been performed by using density functional theory at B3LYP/LANL2DZ level. Herein, we report the experimental results as well as the theoretical calculated results of the title complex.

Experimental Section and Computational Method

All chemicals were obtained from a commercial source and used without further purification.

Synthesis. (5,10,15,20-Tetraphenylporphyrinato)cadmium(II) (CdTPP) was prepared by the reaction between cadmium acetate and 5,10,15,20-tetraphenylporphyrin in *N*,*N'*-dimethylformamide according to the literature.[9] Then, Cd(TPP) (0.149 g, 0.205 mmol) was dissolved in *N*,*N'*-dimethylformamide (50 mL), stirred, and α-aminopyridine (0.0193 g, 0.205 mmol) was added. After the mixture was refluxed with stirring for 10 h, the dark-green solution was reduced to dryness in vacuo, and the residue was redissolved in acetone (50 mL) to obtain green solution. This green solution was filtered and the filtrate was left to stand undisturbed. The dark-blue rhombuses of the title complex were obtained by slow evaporation of acetone at room temperature for several days. Yield: 94%. Elemental analysis calc. for $C_{52}H_{40}CdN_6O$: C, 71.19; H, 4.60; N, 9.58%. Found: C, 71.01; H, 4.38; N, 9.39%. IR ν 3447 (vs), 3097 (m), 1624 (s), 1596 (s), 1491 (m), 1441 (m), 1331 (m), 1267 (m), 1199 (m), 1066 (m), 1006 (m), 992 (s), 792 (s), 751 (m), 702 (s) cm^{-1}.

X-ray structure determination. The selected crystal of $[Cd(TPP)(C_5H_6N_2)]\cdot CH_3(CO)CH_3$ was mounted on a Rigaku Raxis-IV diffractometer. Reflection data were measured at 20 °C using graphite monochromated Mo-K_α (λ = 0.71073 Å) radiation and a ω-2θ scan mode. A total of 8791 independent reflections were collected in the range of $1.42 < \theta < 24.97°$, of which 6477 reflections with $I > 2\sigma(I)$ were considered to be observed and used in the succeeding refinement. The correction for *Lp* factors and empirical absorption were applied to the data. The structure was solved by direct methods and refined by full-matrix least-squares method on F_{obs}^2 using the SHELXTL software package.[10] All non-H atoms were anisotropically refined. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent C atoms. The final least-square cycle gave $R = 0.0387$, $R_w = 0.0998$; the weighting scheme, $w = 1/[\sigma^2(F_o^2) + (0.0660P)^2 + 0.5605P]$, where $P = (F_o^2 + 2F_c^2)/3$. Atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-Ray Crystallography.[11]

Crystallographic data for the structure reported here have been deposited with CCDC (Deposition No. CCDC-279682). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, email: deposit@ccdc.cam.ac.uk.

Results and Discussion

Crystal structure. The title complex crystallizes in triclinic system, space group *P*-1, with lattice parameters *a* =

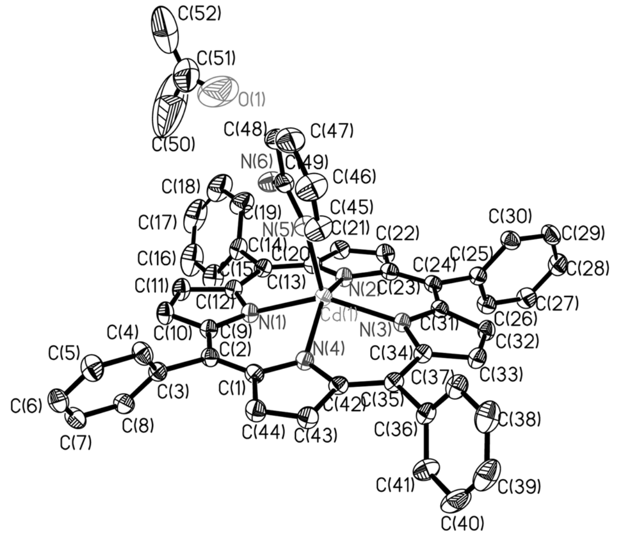
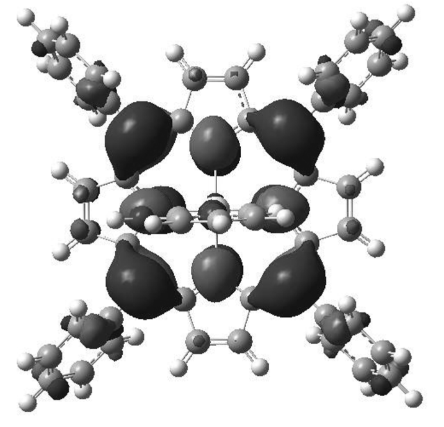


Figure 1. OPTER diagram of $[Cd(TPP)(C_5H_6N_2)]\cdot CH_3(CO)CH_3$ with 35% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

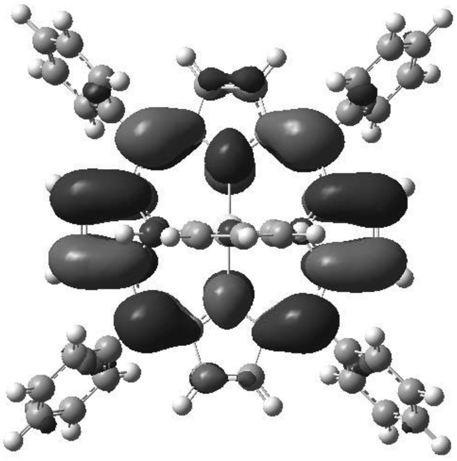
11.331(2) Å, b = 13.275(3) Å, c = 15.160(3) Å, α = 107.72(3)°, β = 95.28(3)°, γ = 95.36(3)°, V = 2145.1(7) Å^3, Mr = 877.30 ($C_{52}H_{40}CdN_6O$), Z = 2, D_c = 1.358 g/cm^3, μ = 0.555 mm^{-1}, F(000) = 900, R = 0.0387, wR = 0.0998. A displacement ellipsoid plot, with the numbering scheme, is shown in Figure 1.

The unit cell is made up of two isolated $[Cd(TPP)(C_5H_6N_2)]$ molecules and two acetone molecules of solvation (Figure 1) separated by ordinary Van der Waals distances. The Cd^{2+} ion of the $[Cd(TPP)(C_5H_6N_2)]$ molecule has a five-coordinate geometry of metalloporphyrin complex,[12,13] which can be described as a distorted square-pyramid. The basal coordination positions are occupied by four pyrrole nitrogen atoms and the axial position is achieved by linking to a nitrogen atom of α-aminopyridine. Four Cd-N(pyrrole) distances range from 2.197(2) to 2.214(2) Å, which are typical Cd-N bond lengths.[13] Cd-N(axial) distance [2.315(3) Å] is smaller than that found in the similar structure with five-coordination geometry of Cd(TPP)·piperidine [2.323(3) Å].[13] The bond lengths and bond angles in phenyl rings, pyrrole rings, α-aminopyridine and acetone are all in the normal range. The porphrin core (24 atoms) is not a plane, with torsion angles of −2.79(3), 4.42(3), 5.64(3) and 7.11° for N(1)-C(12-C(13)-C(20), N(2)-C(23)-C(24)-C(31), N(3)-C(34)-C(35)-C(42) and N(4)-C(1)-C(2)-C(9), respectively. The phenyl rings are almost planar and are oriented almost perpendicular to the porphyrin ring at angles from 60.53 to 75.43°. The axial α-aminopyridine molecule is also oriented almost vertical to the porphyrin with the angle of 81.63°.

In the crystal lattice, there is one intrermolecular hydrogen bond between carbonyl oxygen O(1) of acetone and amino-nitrogen N(6) of α-aminopyridine, with the hydrogen bond distance being 2.9546 Å, and bond angle being 168.02° [symmetry code : x, y, 1+z], which stabilizes the structure.



HOMO



LUMO

Figure 2. The surfaces of HOMO and LUMO for $[Cd(TPP)(C_5H_6N_2)]$.

Electronic spectra. The electronic absorption spectra of the title compound in a solution of acetone exhibit one intense band at 428.9 nm (log ε = 3.01). Natural Bond Orbital (NBO) analyses based on the optimized geometry using density functional theory at B3LYP/LANL2DZ level indicates that the frontier molecular orbitals of the title complex are mainly composed of p atomic orbitals, so above electronic transition is mainly derived from the contribution of bands $\pi \rightarrow \pi^*$. Figure 2 shows the surfaces of HOMO (the highest occupied molecular orbital) and LUMO (the lowest unoccupied molecular orbital). Seen from Figure 2, the HOMO of the title complex is principally delocalized among four pyrrole nitrogen atoms and four carbons connecting two pyrroles and one phenyl ring, while the LUMO is mainly delocalized on four carbons connecting two pyrroles and one phenyl ring, two pyrrole nitrogen atoms and four carbons coming from the other two pyrrole molecules. Both the central Cd(II) ion and the axial α-aminopyridine molecule do not take part in the formation of the HOMO and LUMO.

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