研究简报

# 二{桥-2,4,6-三[二(2-吡啶基)胺]-1,3,5-三嗪-*N*,*N*′,*N*″,*N*‴}·四氯合二锌(Ⅱ)的合成与晶体结构

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**关键词**:锌(Ⅱ);双核配合物;1,3,5-三嗪衍生物;晶体结构
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## Synthesis and Crystal Structure of Bis{$\mu_2$-2,4,6-tris[bis(2-pyridyl)amine]-1,3,5-triazine-*N*,*N*′,*N*″,*N*‴}- tetrachloro-di-zinc(Ⅱ)

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**Abstract:** A dinuclear Zn(Ⅱ) complex $C_{66}H_{48}Cl_4N_{24}Zn_2\cdot 2CH_3OH\cdot 2H_2O$ (**1**) was synthesized and characterized by X-ray crystallography. In the complex, two 2,4,6-tris[bis(2-pyridyl)amino]-1,3,5-triazine ligands are bridged together by two zinc(Ⅱ) ions and stacked in a parallel manner. CCDC: 267649.

**Key words:** zinc(Ⅱ); dinuclear complex; 1,3,5-triazine derivative; crystal structure

The derivatives of 1,3,5-triazine are a class of important polydentate ligands that offer the potential to bind multi-metal ions in a certain preorganized trigonal spatial arrangement[1]. These compounds and the related metal complexes could provide versatility and diversity for supramolecular assembly and hence have been studied extensively in the past few years[2,3]. Moreover, due to the structural similarity of the parental 1,3,5-triazine ring to purine and pyrimidine, these ligands have attracted wide attention for the exploration of biological properties[4-6]. We report herein the synthesis and crystal structure of a 1,3,5-triazine derived dizinc complex (**1**), in which two 2,4,6-tris[bis(2-pyridyl)amino]-1,3,5-triazine (TBAT) ligands are pulled together by two zinc ions in a parallel mode. The molecular structure of **1** is drawn in Fig.1.

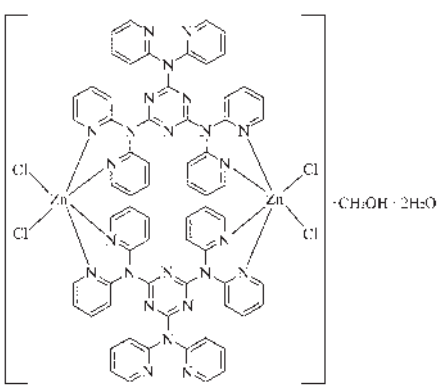


Fig.1 Molecular structure of complex **1**

## 1 Experimental

### 1.1 Syntheses

The ligand TBAT was synthesized from 2,4,6-

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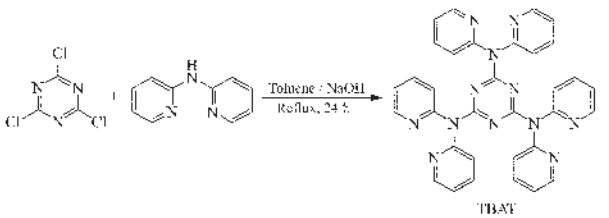
trichloro-1,3,5-triazine and 2,2′-pyridylamine according to a previously published procedure (Scheme 1)[7]. Complex **1** was prepared as follows: a suspension of TBAT (589 mg, 1.00 mmol) in acetonitrile (15 mL) was added dropwise to a solution of $ZnCl_2$ (136.3 mg, 1.00 mmol) in methanol (15 mL) under stirring; colorless crystalline compound (868 mg) was formed, isolated and dried. Single crystals suitable for X-ray analysis were obtained by slow diffusion between two layers of the methanol/water solution (5/1, *V*/*V*) and dichloromethane at room temperature for several days. Yield: 59%. Anal. Calcd for $C_{68}H_{58}Cl_4N_{24}O_4Zn_2$ (%): C, 52.76; H, 3.78; N, 21.72. Found (%): C, 52.52; H, 3.68; N, 21.58. FTIR ($cm^{-1}$): 3 424.8 (br, w), 3 054.7 (w), 3 010.1 (w), 1 642.9 (w), 1 589.4 (s), 1 539.5 (s), 1 462.5 (s), 1 433.1 (m), 1 482.9 (s), 1 312.6 (m), 1 291.5 (m), 1 251.6 (w), 1 135.7 (w), 779.2 (w), 744.1 (w), 667.6 (w).




Scheme 1 Synthesis of TBAT

### 1.2 Determination of crystal structure

A block single crystal of **1** with approximate dimensions of 0.3 mm × 0.3 mm × 0.3 mm was selected for X-ray diffraction analysis. The diffraction data were collected at 293 K on a Bruker Smart Apex CCD area detector using graphite monochromatized Mo $K\alpha$ radiation ($\lambda$=0.071 073 nm) by $\varphi$-$\omega$ scans. The collected data were reduced using the SAINT program and empirical absorption correction was carried out using the SADABS program. The structure was solved by direct methods using the SHELXTL-XS program. Refinement was made by full-matrix least-square method on $F^2$ using the SHELXTL-XL program for all data with anisotropic thermal parameters for non-hydrogen and isotropic parameters for hydrogen atoms[8]. The crystal structure data and refinement parameters of complex **1** are shown in Table 1.

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**Table 1 Crystallographic data and refinement parameters of complex 1**

| | | | |
|---|---|---|---|
| Formula | $C_{66}H_{48}Cl_4N_{24}Zn_2\cdot 2CH_3OH\cdot 2H_2O$ | $\theta$ range for data collection / (°) | 2.0~26.0 |
| $M_r$ | 1 549.94 | Index ranges | $-16 \leqslant h \leqslant 11$, $-16 \leqslant k \leqslant 17$, $-27 \leqslant l \leqslant 26$ |
| Temperature / K | 293 | Reflections collected/unique | 7 595 / 6 533 [$R_{int}$=0.033] |
| Crystal system | Monoclinic | $F$(000) | 1 592 |
| Space group | $P2_1/c$ | $\mu$ / $mm^{-1}$ | 0.817 |
| $a$ / nm | 1.347(2) | Max. and min. transmission | 0.82 and 0.78 |
| $b$ / nm | 1.434(2) | Data / restrains / parameters | 7 595 / 0 / 470 |
| $c$ / nm | 2.219(3) | Goodness-of-fit on $F^2$ | 1.084 |
| $\beta$ / (°) | 115.17(6) | Refinement method | Full-matrix least-squares on $F^2$ |
| $V$ / $nm^3$ | 3.878(9) | $R$ indices [$I>2\sigma$] | $R_1$=0.049 6, $wR_2$=0.143 2 |
| $Z$ | 2 | $R$ indices (all data) | $R_1$=0.059 3, $wR_2$=0.147 7 |
| $D_c$ / ($g\cdot cm^{-3}$) | 1.327 | Largest diff. peak and hole / ($e\cdot nm^{-3}$) | 580 and −640 |
| Crystal size / mm | 0.24 × 0.26 × 0.30 | | |

## 2 Results and discussion

Complex **1** crystallizes in a monoclinic $P2_1/c$ space group with a molecular formula of $C_{66}H_{48}Cl_4N_{24}Zn_2\cdot 2CH_3OH\cdot 2H_2O$. The crystal structure of **1** with the atom labeling scheme is shown in Fig.2 and the selected bond lengths and angles are given in Table 2. The X-ray crystallographic study shows that **1** contains two hexa-coordinated zinc atoms that distort slightly from the octahedral geometry. Specifically, the distorted octahedral geometry was formed by two pyridyl-N atoms from different TBAT ligands at axial positions and two other pyridyl-N atoms from different TBAT and two Cl atoms at equatorial positions. The distortion is due to the twisted coordination of the rigid TBAT ligands. The axial angle N1-Zn1-N5A is 179.1(1)°. Among the four equatorial angles around the zinc atom, angle N2-Zn1-N4A [101.9(2)°] is larger than the other three angles Cl1-Zn1-N4A, Cl1-Zn1-Cl2 and Cl2-Zn1-N2

**Table 2　Selected geometric parameters (nm, °)**

| | | | | | |
|---|---|---|---|---|---|
| Zn1-Cl1 | 0.213 4(3) | Zn1-N1 | 0.210 4(4) | Zn1-N4A | 0.207 8(4) |
| Zn1-Cl2 | 0.208 7(3) | Zn1-N2 | 0.207 3(4) | Zn1-N5A | 0.206 4(4) |
| N1-Zn1-N5A | 179.1(1) | N2-Zn1-N5A | 91.0(1) | Cl2-Zn1-N2 | 86.1(1) |
| N1-Zn1-N2 | 88.3(1) | N4A-Zn1-N5A | 89.6(1) | Cl1-Zn1-Cl2 | 86.3(7) |
| N1-Zn1-N4A | 91.1(1) | Cl1-Zn1-N5A | 90.3(1) | Cl1-Zn1-N4A | 85.6(1) |
| Cl1-Zn1-N1 | 90.3(1) | Cl2-Zn1-N5A | 92.7(1) | | |
| Cl2-Zn1-N1 | 86.7(1) | N2-Zn1-N4A | 101.9(2) | | |

**Table 3　Hydrogen-bond geometry (nm, °)**

| D–H···A | D-H | H···A | D···A | D–H···A |
|---|---|---|---|---|
| O1–H1A···O2 | 0.084 0 | 0.255 0 | 0.316 9(8) | 132.00 |
| O2–H2D···O1 | 0.085 0 | 0.232 0 | 0.316 9(8) | 180.00 |
| O3–H3C···O2 | 0.085 0 | 0.251 0 | 0.335 9(8) | 172.00 |
| C1–H1···Cl1 | 0.093 0 | 0.268 0 | 0.313 2(6) | 111.00 |
| C4–H4···O2 | 0.093 0 | 0.245 0 | 0.336 8(8) | 168.00 |
| C12–H12···N1 | 0.093 0 | 0.259 0 | 0.308 8(7) | 114.00 |
| C22–H22···Cl2 | 0.093 0 | 0.260 0 | 0.311 3(6) | 115.00 |

(*ca* 86°). The sum of the four angles is 359.9°, typical for the ideal octahedral value of 360°. The equatorial Zn-N length is 0.207 3 nm and 0.207 8 nm respectively, which is comparable to the Ni-N bond distances in a similar dinuclear nickel (Ⅱ) complex of TBAT [0.206 5(2) nm, 0.208 2(2) nm and 0.209 9(2) nm][9]. Compared with a square-pyramidal trinuclear copper (Ⅱ) complex of TBAT, the Zn-N bond length is somewhat longer than that of Cu-N [0.201 6(4)~0.203 7(4) nm], but the equatorial Zn-Cl bond length [0.213 4(3) nm and 0.208 7(3) nm] is shorter than that of Cu-Cl [0.238 2(1)~0.240 7(1) nm] in the trinuclear copper(II) complex[10]. The axial bond length of Zn-N in **1** is 0.206 4(4) nm and 0.210 4(4) nm respectively, which is comparable to that of the equatorial Zn-N length, and also, to the axial Zn-N bond length in a tetranuclear zinc complex with the same coordination geometry [0.214 6(2) and 0.214 0(0) nm][11]. In short, all the bond lengths and angles in complex **1** are within the normal ranges for this type of geometry. Two disordered water molecules and two methanol molecules are co-crystallized with the neutral complex nucleus.

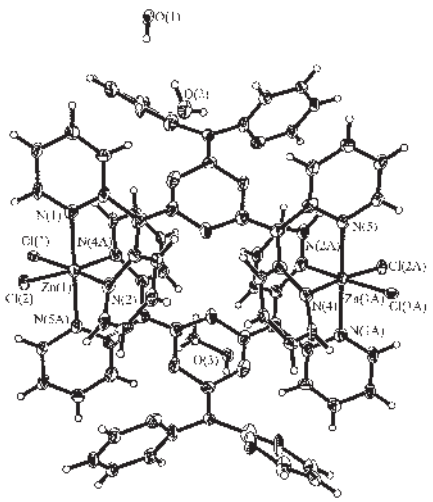


Fig.2　Crystal structure of complex **1** with the selected atomic numbering scheme
The displacement ellipsoids are drawn at the 30% probability level.

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