

双核 Cd(II)配合物 $[\text{Cd}_2(\text{C}_{22}\text{H}_{14}\text{N}_4)_2\text{Cl}_2(\text{N}_3)_2]_2 \cdot \text{H}_2\text{O}$ 的合成与晶体结构

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Synthesis and Crystal Structure of a Dinuclear Cadmium Complex $[\text{Cd}_2(\text{C}_{22}\text{H}_{14}\text{N}_4)_2\text{Cl}_2(\text{N}_3)_2]_2 \cdot \text{H}_2\text{O}$

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Abstract: A dinuclear Cd(II) complex $[\text{Cd}_2(\text{N}_3)_2\text{L}_2\text{Cl}_2]_2 \cdot \text{H}_2\text{O}$ (**1**) [$\text{L}=4'-(4\text{-cyanophenyl})-2,2':6',2''\text{-terpyridine}$] was synthesized by reaction of ligand **L** with CdCl_2 and NaN_3 using solvothermal method and its structure was determined by X-ray crystal structure analysis. The structure indicates that the complex crystallizes in monoclinic, space group $C2/c$ with $a=1.644\ 5(16)$ nm, $b=1.441\ 9(12)$ nm, $c=1.918\ 1(18)$ nm, $\beta=100.349(11)^\circ$. $V=4\ 474(7)$ nm³, $Z=2$, $D_c=1.570$ Mg \cdot m⁻³, $\mu=1.120$ mm⁻¹, $F(000)=2\ 100$, and final $R_1=0.039\ 3$, $wR_2=0.081\ 1$. The result shows a Cd(II) ion was six-coordinated by a tridentate $4'-(4\text{-cyanophenyl})-2,2':6',2''\text{-terpyridine}$ ligand and one bridging nitrogen atom of the azide group in the basal position and an chloride atom and the other bridging nitrogen atom of the azide group in the axialone, to form a distorted octahedral-pyramidal geometry. CCDC: 673291.

Key words: terpyridine; crystal structure; dinuclear cadmium complex

Polypyridine ligands have played an important role in many areas. In particular, the chelating ligand terpyridine and its functionalized derivatives have been studied extensively as outstanding complexing agents for a wide range of metal ions^[1]. As a tridentate ligand, $2,2':6',2''\text{-terpyridine}$ (terpy) forms stable complexes by chelating a broad variety of transition metal ions. Some of these complexes are well known for their potential uses in the design of luminescent devices^[2,3] or applications to chemical sensing^[4-7] and the construction of supramolecular architectures^[8]. The synthesis of function-

alized $2,2':6',2''\text{-terpyridine}$ -terpyridines was recently reviewed by Fallahpour^[9] as well as Heller^[10]. $4'$ -substituted $2,2':6',2''\text{-terpyridines}$ have received major attention due to their symmetry, which prevents the formation of enantiomers upon complexation. The substituted terpyridines have been reported to form a six-coordinate complex with cadmium(II) acetate^[11]. In this paper, we report the crystal structure of the title compound obtained by the solvothermal reaction of $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ and NaN_3 and tridentate $4'-(4\text{-cyanophenyl})-2,2':6',2''\text{-terpyridine}$ ligand.

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1 Experimental

1.1 General procedures

All chemicals were reagent grade and used as received. All solvents were of analytical grade and used directly. The 4'-(4-cyanophenyl)-2,2':6',2''-terpyridine ligand was synthesized according to the method of literature^[12]. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C analyzer. The IR spectra were taken on a Vector22 Bruker Spectrophotometer ($400\sim4\,000\text{ cm}^{-1}$) with KBr pellets.

1.2 Synthesis of complex

A mixture of 4'-(4-cyanophenyl)-2,2':6',2''-terpyridine (30 mg, 0.09 mmol), $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ (23 mg, 0.1 mmol), NaN_3 (20 mg, 0.31 mmol), 1.5 mL 15% water-ethanol in a sealed glass tube was kept at $120\text{ }^\circ\text{C}$. Colorless crystals suitable for X-ray diffraction were obtained after 5 days. Elemental analysis calculated for $\text{C}_{88}\text{H}_{58}\text{Cd}_4\text{Cl}_4\text{N}_{28}\text{O}$ (%): C, 49.97; H, 2.76; N, 18.54. found (%): C, 49.89; H, 2.81; N, 18.48. IR (KBr) (cm^{-1}): 3 389; 2 227; 2 042; 1 399; 638.

1.3 Crystal structure determination

A red single crystal with dimensions of $0.30\text{ mm} \times$

$0.26\text{ mm} \times 0.24\text{ mm}$ was selected for X-ray structure analysis. The data were collected on a Rigaku SCX Mini CCD diffractometer using a graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$) at $291(2)\text{ K}$. A total of 22 007 reflections were collected in the range of $3.01^\circ \leq \theta \leq 27.46^\circ$ by using an ω - 2θ scan mode, of which 5 096 were unique with $R_{\text{int}}=0.039\,7$. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques using the SHELXS-97 and SHELXL-97 program^[13,14]. All of the non-hydrogen atoms were refined for 3 778 observed reflections with $I>2\sigma(I)$ to give the final $R=0.039\,3$, $wR=0.081\,1$ ($w=1/[\sigma^2(F_o^2)+(0.033\,3P)^2+1.586P]$, where $P=(F_o^2+2F_c^2)/3$, $S=1.05$. Positional parameters of all the H atoms were calculated geometrically and were allowed to ride on their respective parent atoms, with $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$ or $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{O})$. The highest peak and deepest hole in the final difference Fourier map are 388 and $-567\text{ e}\cdot\text{nm}^{-3}$, respectively. Crystal data and structure refinement for the title complex are listed in Table 1.

CCDC: 673291.

Table 1 Crysta data amd structure refinement parameters for the title complex

Empirical formula	$\text{C}_{88}\text{H}_{58}\text{Cd}_4\text{Cl}_4\text{N}_{28}\text{O}$	$F(000)$	2100
Formula weight	2 115.06	Crystal size / mm	$0.30 \times 0.26 \times 0.24$
T / K	291	θ range for data collection / ($^\circ$)	$3.01\sim27.46$
Crystal system	Monoclinic	Index ranges	$-21 \leq h \leq 21, -18 \leq k \leq 18, -24 \leq l \leq 24$
Space group	$C2/c$	Reflections collected / unique	22 007 / 5 096 ($R_{\text{int}}=0.040$)
a / nm	1.644 5(16)	Refinement method	Full-matrix least-squares on F^2
b / nm	1.441 9(12)	Data / restraints / parameters	5 096 / 2 / 295
c / nm	1.918 1(18)	Goodness-of-fit on F^2	1.053
$\beta / (^\circ)$	100.349(11)	R_1 (on F) [$I>2\sigma(I)$]	0.039 3
Z	2	wR_2 (on F^2) [$I>2\sigma(I)$]	0.081 1
$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.57	Largest diff. peak and hole / ($\text{e}\cdot\text{nm}^{-3}$)	388 and -567
μ / mm^{-1}	1.12	Absorption correction	Multi-scan

2 Results and discussion

2.1 Structural analysis

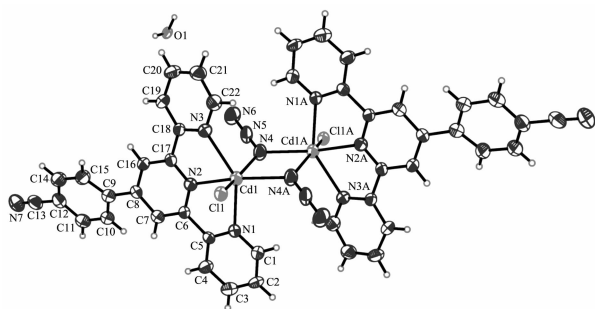
An ORTEP drawing of the structure with atomic numbering are shown in Fig.1. X-ray crystal structure analysis of complex **1** reveals that the crystallographic unit of the title complex consists of two Cd(II) ions, two

azide anions, two 4'-(4-cyanophenyl)-2,2':6',2''-terpyridine and one water molecules in which the two Cadmium (II) ions are bridged by two end-on azide groups. The selected bond lengths and angles of this compound are listed in Table 2.

The Cd(II) center is six-coordinated with a slightly distorted octahedral geometry. The equatorial positions

Table 2 Selected bond lengths (nm) and bond angles (°) for the title complex

Cd1-N1	0.239 0(3)	Cd1-N4	0.247 2(3)	N4-N5	0.114 5(4)
Cd1-N2	0.231 4(3)	Cd1-N4(A)	0.226 8(3)	N5-N6	0.119 3(4)
Cd1-N3	0.235 3(3)	Cd1-Cl1	0.265 8(2)	C13-N7	0.115 0(5)
N3-Cd1-N4	81.89(11)	N3-Cd1-Cl1	92.72(9)	N4(A)-Cd1-N1	96.82(10)
N4-N5-N6	176.8(4)	N2-Cd1-Cl1	108.28(9)	N2-Cd1-N3	69.66(10)
Cd1(A)-N4-Cd1	105.12(13)	N4(A)-Cd1-Cl1	92.89(10)	N4(A)-Cd1-N2	156.35(10)
N5-N4-Cd1	122.8(2)	N2-Cd1-N4	86.84(11)	N4(A)-Cd1-N3	120.99(11)
N5-N4-Cd1(A)	124.9(2)	N4(A)-Cd1-N4	74.88(13)	N1-Cd1-N4	95.92(10)
N4-Cd1-Cl1	161.17(8)	N3-Cd1-N1	139.52(9)	N1-Cd1-Cl1	99.77(7)
N2-Cd1-N1	69.86(9)				

Symmetry code: (A) $-x+1/2, -y+1/2, -z+2$.Displacement ellipsoids are drawn at the 30% probability level; symmetry code: A: $-x+1/2, -y+1/2, -z+2$ **Fig.1** Structure of the title compound with the atomic numbering scheme

are occupied by the three nitrogen atoms of 4'-(4-cyanophenyl)-2,2':6',2''-terpyridine ligand and a nitrogen atom from a bridging azide group. In the axial position, one chlorine atom and the other nitrogen atom from the azide bridging group, belonging to the other of the dimer, complete the coordination sphere. The end-on azides are located upwards and downwards from the bridge plane, respectively. There is also one crystallization molecules of water per dimeric unit. The *cis* N-Cd-N angle range from 69.65(11)° to 139.49(9)° while the largest deviation from linearity in the trans angles is observed for N2-Cd-N4(156.41(11)°). As can be seen in Table 2 for the title compound, the bridge between metallic cations shows two significantly different distances (Cd-N4 and Cd-N4(A) (A: $-x+1/2, -y+1/2, -z+2$) 0.226 8(3) nm and 0.247 3(3) nm, respectively), The interior N(4)-Cd-N4(A) angle of the bridging arrangement is 74.91(13)° while the Cd1-N4-

Cd1(A) bridge-angle being 105.09(13)°. The distance between metallic cations and Cl ion is intermediate between the Cd-Cl distances (Cd-Cl1 0.265 8(2) nm). The dimer sits on an inversion center, hence the Cd2N2 bridging unit is planar. The Cd1-Cd1(A) distance is 0.376(6) nm, which is significantly larger than the sum of the two Cadmium radii (0.109 nm for Cd(II)) and precludes any direct Cd-Cd bonding.

The three pyridyl rings are approximately coplanar, with interplanar angles of 7.72° (between ring N3/C18-C22 and the central pyridyl ring), 3.85° (between ring N1/C1-C5 and the central pyridyl ring) and adopt the transoid arrangement which minimizes interactions between nitrogen lone pairs. While the pendant substituted phenyl rings are twisted away from coplanarity with the adjacent terpyridyl unit and forms dihedral angles of 23.39°. The Cd-N distance to the central pyridine ring is significantly shorter than the distances to the outer pyridine rings as a result of steric interactions, further indicating a compressed octahedral geometry. The lateral pyridine N-Cd distance is 0.235 3(3) nm (N3-Cd1) and 0.239 0(4) nm (N1-Cd1) respectively; while the middle pyridine Cd1-N2 distance is 0.231 1(3) nm, similar to the previous Cadmium(II) bis-complex of a terpyridine ligand^[11]. The C-C and C-N bond lengths within the aromatic rings are normal (C-C distances range from 0.134 7(5) to 0.144 4(6) nm and C-N distances from 0.133 5(5) to 0.136 3(4) nm). These bond lengths are similar to those observed for other cadmium polypyridyl complexes^[11,15-17]. In the crystal

structure, there are no evidence that was observed for the existence of intermolecular aromatic π - π stacking interactions between the terpyridyl unit molecules arranged in the trans~trans conformation.

2.2 IR spectroscopy

The major interest of the IR spectra of the title compounds is the bonds corresponding to the azide groups. The title Compounds shows one intense IR absorptions at $2\,042\text{ cm}^{-1}$ which can be assigned to the antisymmetric stretch of the bridging azide group (ν_{asym}). Two signals at $1\,399$ and 638 cm^{-1} can be observed, corresponding to the azide symmetry stretch and the azide bending vibration respectively. A absorption at $2\,227\text{ cm}^{-1}$ is ascribed to the $\text{C}\equiv\text{N}$ stretching vibration. Finally, the IR spectrum exhibits a broad signal at $3\,400\text{ cm}^{-1}$ which can be associated to the crystallization molecule of water.

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