第 25 卷第 8 期
2009 年 8 月

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CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol.25 No.8
1504~1507

研究简报

一维链状铜配合物的合成及结构表征

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关键词:铜配合物;三联吡啶;晶体结构;一维链

中图分类号:O614.121 **文献标识码**:A **文章编号**:1001-4861(2009)08-1504-04

Synthesis and Crystal Structure of Cu(Ⅰ) Complex with One-Dimensional Chain Structure

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Abstract: The Copper (Ⅰ) complex $[Cu(tpy)(CN)]_n$ [L=4′-(4-cyanophenyl)-2,2′:6′,2″-terpyridine] has been synthesized by reaction of ligand L with CuCN using solvothermal method and characterized by IR, elemental analysis and X-ray diffraction single-crystal structure analysis. The crystal structure indicates that the complex crystallizes in monoclinic system, space group $P2_1/c$ with a=0.884 45(18) nm, b=0.819 55(16) nm, c=2.702 90(7) nm, β=102.780(3)°, V=1.910 7(7) nm^3, Z=4, D_c=1.495 g·cm^{-3}, F(000)=864.0, R_1=0.059 3, wR_2=0.123 3. The Cu(Ⅰ) ion in the title complex has a slightly distorted tetrahedron coordination geometry. Each Cu^+ is coordinated with two nitrogen atoms from two pyridine ring of 4′-(4-cyanophenyl)-2,2′:6′,2″-terpyridine, and then linked by two CN^- ligands with neighbor Cu^+ forming a zigzag infinite one-dimensional chain structure. CCDC: 686952.

Key words: Cu(Ⅰ) complex; terpyridine; crystal structure; one-dimensional chain

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″-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 construc-tion of supramolecular architectures [8]. The synthesis of functionalized 2,2′:6′,2″-terpyridines was recently reviewed by Fallahpour[9] as well as Heller[10]. 4′-substituted 2,2′:6′,2″-terpyridines have received major attention due to their symmetry, which prevents the formation of enantiomers upon complexation. Recently we have reported the syntheses and crystal structures of new dinuclear cadmium complex with 4′-(4-cyanophenyl)-2,2′:6′,2″-terpyridine ligand[11]. As a continuation of our investigation of this ligand, here we report the

收稿日期:2009-02-16。收修改稿日期:2009-06-05。

东南大学启动基金资助项目。

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crystal structure of the title compound obtained by the solvothermal reaction of CuCN and tridentate 4′-(4-cyanophenyl)-2,2′:6′,2″-terpyridine ligand.

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 (400~4 000 cm^{-1}) with KBr pellets.

1.2 Synthesis of complex

A mixture of 4′-(4-cyanophenyl)-2,2′:6′,2″-terpyridine (20 mg, 0.06 mmol), CuCN (25 mg, 0.27 mmol), 1.5 mL 10% water-ethanol in a sealed glass tube was kept at 80 ℃. Colorless crystals suitable for X-ray structure analysis were obtained after 4 days. Elemental analysis calculated for $C_{23}H_{14}CuN_5$ (%): C, 65.16; H, 3.33; N, 16.52. found (%): C, 65.08; H, 3.35; N, 16.45. IR (KBr / cm^{-1}): 2 226; 2 114; 790; 740, 685.

1.3 Crystal structure determination

A red single crystal with dimensions of 0.15 mm×0.17 mm×0.25 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 (λ=0.071 073 nm) at 293(2) K. A total of 15 865 reflections were collected in the range of 3.09° ≤θ≤25.50° by using an ω-2θ scan mode, of which 3 558 were unique with R_{int}=0.086 0. 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]. Because of symmetry-required disorder of bridging cyanides, each atom was represented by 'CN' and assigned as a half N and a half C. Positional parameters of all the H atoms were calculated geometrically and were allowed to to ride on their respective parent atoms, with U_{iso}(H)=1.2U_{eq}(C). All of the non-hydrogen atoms were refined by full-matrix least-squares techniques for 3 558 unique reflections and 2 395 observed reflections with $I>2\sigma(I)$. The highest peak and deepest hole in the final difference fourier map are 653 and −334 e·nm^{-3}, respectively. Crystallographic data and details of data collection and structure refinement for the title complex are listed in Table 1.

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

Empirical formula	$C_{23}H_{14}CuN_5$	F(000)	864
Formula weight	423.93	Crystal size / mm	0.15×0.17×0.25
T / K	293(2)	θ range for data collection / (°)	3.09~25.50
Crystal system	Monoclinic	Index ranges	$-10 \leqslant h \leqslant 10, -9 \leqslant k \leqslant 9, -32 \leqslant l \leqslant 32$
Space group	$P2_1/c$	Reflections collected / unique (R_{int})	15 865 / 3 558 (0.0860)
a / nm	0.884 45(18)	Absorption correction	Multi-scan
b / nm	0.819 55(16)	Refinement method	Full-matrix least-squares on F^2
c / nm	2.702 90(7)	Data/restraints/parameters	3 558 / 48 / 262
β / (°)	102.780(3)	Goodness-of-fit on F^2	1.068
Z	4	R_1, wR_2 (all data)	0.097 7, 0.135 4
D_c / (g·cm^{-3})	1.474	R_1, wR_2 [$I>2\sigma(I)$]	0.059 3, 0.123 3
μ / mm^{-1}	1.162	Largest diff. peak and hole / (e·nm^{-3})	653 and −334

2 Results and discussion

2.1 Structural analysis

The ORTEP drawing of the structure along with the atom-numbering scheme is shown in Fig.1. The crystal structure of complex **1** reveals that the crystallographic unit of the title complex consists of one Cu(I) ions, two cyanides anions, one 4′-(4-cyanophenyl)-2,2′:6′,2″-terpyridine. Each copper ion is coordinated by two cyanide groups and two nitrogen atom of 4′-(4-

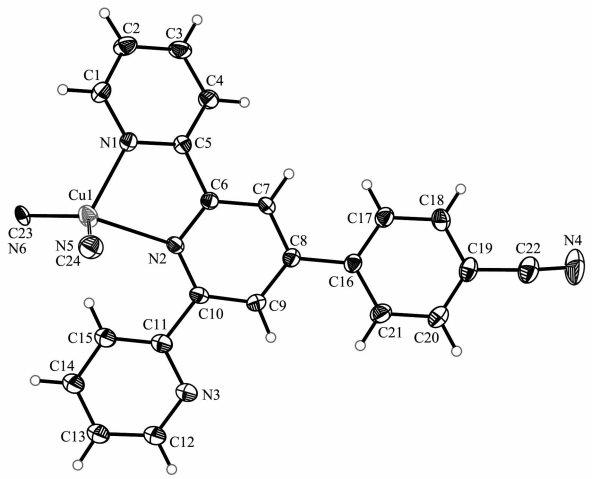

Fig.1 ORTEP view of asymmetric unit of the title compound, displacement ellipsoids are drawn at the 30% probability level

cyanophenyl)-2,2′ :6′ ,2″ -terpyridine. Bond distances and angles are listed in Table 2. Interestingly, one nitrogen of terpyridine ligand don′t coordinate with metal ion which form a bidentate terpyridine. The two nitrogen atoms of the 4′-(4-cyanophenyl)-2,2′:6′,2″-terpyridine coordinates to the Cu(I) atom to form one five-membered chelate ring. The five-membered ring displays an envelope conformation, with the Cu(I) atom in the flap position and deviating from the mean plane formed by the other four atoms by 0.057 6 nm. In the five-membered chelate ring, the Cu-N distances are unequal with Cu-N1, 0.205 7(3) nm and Cu-N2, 0.239 3(3) nm. This has been observed in other complexes involving bidentate terpy[15]. The presence of uncoordinated pyridine ring gives rise to steric interactions which result in significantly longer Cu-N2 bond compared to the Cu-N1. Compared to the angle of ideal tetrahedron is 109.28°, while the cis N-Cu-N and N-Cu-C angle range from 75.38 (12)° to 125.92 (17)° and the coordination environment around each Cu (I) center significantly deviates from an ideal tetrahedron which can be best described as severely distorted tetrahedron.

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

Cu1-N5	0.189 2(3)	N1-C1	0.133 8(5)	N4-C22	0.112 2(6)
Cu1-C23	0.194 4(4)	N1-C5	0.134 3(5)	C11-N3	0.134 4(6)
Cu1-N1	0.205 7(3)	N2-C6	0.134 8(5)	N3-C12	0.132 2(6)
Cu1 N2	0.239 3(3)	N2-C10	0.134 8(5)		
N5-Cu1-C23	125.92(17)	N5-Cu1-N2	104.06(15)	N1-Cu1-N2	75.38(12)
N5-Cu1-N1	121.48(16)	C23-Cu1-N2	117.15(15)	C1-N1-Cu1	123.0(3)
C23-Cu1-N1	102.43(15)				

The C-C and C-N bond lengths within the aromatic rings are normal (C-C distances range from 0.135 8(6) to 0.149 7(6) nm and C-N distances from 0.132 2(6) to 0.134 8(5) nm). The Cu1-N5 (0.189 2(3) nm) bond length is significantly shorter than Cu1-N1 (0.205 7(3) nm) and Cu1-N2 (0.239 3(3) nm) which indicating the coordination capability of cyanide group is slightly stonger than the pyridine. The two pyridyl rings (between ring N1/C1-C5 and the central pyridyl ring) where nitrogen atoms are involved in coordination makes an interplanar angle of 29.00(0.17)°, where the non-coordinating pyridyl ring N3/C18-C22 makes an angle of 2.34(0.26)° with respect to the central pyridyl ring and they are approximately coplanar. In addition,

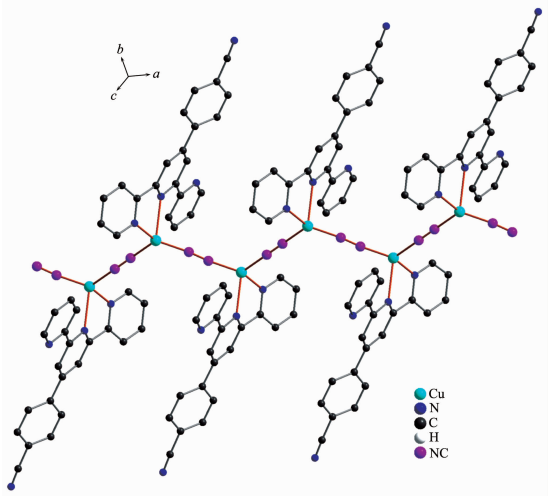

Fig.2 Molecular one-dimensional chain structure of the complex

the pendant substituted phenyl rings C16-C21 are twisted away from coplanarity with the adjacent terpyridyl unit N2/C6-C10 and forms dihedral angles of 22.21(0.22)°.

As shown in Fig.2, The cyanide group act as a μ-bridging ligand that coordinates to two Cu atoms, and two Cu centers connected by two bridging cyanide group ligands with a Cu⋯Cu distance of 0.494 8 nm forming an infinite one dimension zigzig chain structure. In the crystal structure, the terpyridyl unit molecules are 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 cyanide groups. The title compounds shows one intense IR absorptions at 2 226 cm^{-1} which can be assigned to the antisymmetric stretch of the non-coordinating cyanide groups of 4′ -(4-cyanophenyl)-2,2′ :6′ ,2″ -terpyridine, however the signals at 2 114 can be ascribed to the bridging cyanide group (ν_{asym}). Three signals at 790, 740 and 658 cm^{-1} can be observed, corresponding to the bending vibration of the pyridine ring.

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