



## Synthesis and Crystal Structure Analysis of Co(II) Complex with Terpyridine Ligand

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The Co(II) complex,  $[\text{CoL}_2] \cdot [(\text{ClO}_4)_2] \cdot [\text{H}_2\text{O}]$  [L = 4'-(4-cyanophenyl)-2,2':6',2''-terpyridine], has been synthesized by the reaction of tridentate ligand L with  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and its structure was characterized by X-ray crystal structure analysis. The structure indicates that the complex belongs to monoclinic, space group Cc with  $a = 1.4018(12)$  nm,  $b = 1.2223(10)$  nm,  $c = 2.520(2)$  nm,  $\beta = 100.676(9)^\circ$ .  $V = 4.244(6)$  nm<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.479$  Mg m<sup>-3</sup>,  $\mu = 0.598$  mm<sup>-1</sup>,  $F(000) = 1932$  and final  $R_1 = 0.0683$ ,  $wR_2 = 0.1461$ . The result shows a Co(II) ion is six-coordinated by two tridentate 4'-(4-cyanophenyl)-2,2':6',2''-terpyridine ligand and forms a distorted octahedral-pyramidal geometry. The two benzene rings adjacent to the pyridines form dihedral angles of  $31.76(0.32)$  and  $32.36(0.33)^\circ$  with the central pyridine ring systems, respectively. One of the  $\text{ClO}_4$  groups is disordered in two orientation with the site-occupancy factors 0.71 (2) and 0.29 (2). CCDC: 681080.

**Keywords:** Terpyridine, Crystal structure, Co(II) complex.

### INTRODUCTION

Polypyridine ligands have attracted great interest in many fields. 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<sup>1-3</sup>. As a N,N'',N'''-tridentate ligand, 2,2':6',2''-terpyridine (terpy) can usually form stable complexes by chelating a broad variety of transition metal ions. Some of these complexes are well known for their potential applications in the design of luminescent devices<sup>4-7</sup>, the construction of supramolecular architectures<sup>8,9</sup>, the uses to chemical sensors<sup>10-14</sup>, etc. The synthesis of functionalized 2,2':6',2''-terpyridines was also reviewed by Fallahpour<sup>15</sup> as well as Heller and Schubert<sup>16</sup>. 4'-Substituted 2,2':6',2''-terpyridines have received great attention due to the introduction of substituents into the 4'-position of terpyridine which leads to compounds having properties with potential applications in photochemistry<sup>17</sup>, construction of multimetallic arrays<sup>18</sup> and enhancement of spin-crossover behaviors<sup>19,20</sup>. The substituted terpyridines have been reported to form a six-coordinate complex with cobalt(II) acetate<sup>21,25</sup>. We have synthesized 4'-cyanophenyl-2,2':6',2''-terpyridine (cpty) and prepared one cobalt complex of this ligand. In this paper, we will report the crystal structure of the title compound obtained by the reaction of  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  and the tridentate 4'-(4-cyanophenyl)-2,2':6',2''-terpyridine ligand.

### EXPERIMENTAL

All chemicals are reagent grade and used as received. All solvents are of analytical grade and used directly unless otherwise noted. The 4'-(4-cyanophenyl)-2,2':6',2''-terpyridine ligand was synthesized according to the literature<sup>22</sup>. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240 C analyzer. The IR spectra were taken on a Vector22 Bruker Spectrophotometer (4000-400 cm<sup>-1</sup>) with KBr pellets.

**Synthesis of complex:** The mixture of 4'-(4-cyanophenyl)-2,2':6',2''-terpyridine (33.4 mg, 0.1 mmol) and  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (12 mg, 0.11 mmol) in 20 mL methanol was heated to reflux for 1 h. When cooled, 20 mL ethyl ether was added to the solution and the product precipitated was obtained by the filtration. The product was dissolved with acetonitrile and the solution was filtrated. Red crystals suitable for X-ray analysis were obtained by the evaporation of the solution at room temperature after a week. Elemental analysis calculated for  $\text{C}_{44}\text{H}_{30}\text{N}_8\text{O}_9\text{Cl}_2\text{Co}$  (%): C, 55.95; H, 3.20; N, 11.86. found: C, 55.88; H, 3.24; N, 11.91. IR (KBr,  $\nu_{\text{max}}$ , cm<sup>-1</sup>): 2225; 790; 731; 622.

**Crystal structure determination:** A red single crystal with dimensions of 0.15 mm × 0.10 mm × 0.10 mm was selected for X-ray structure analysis. The data were collected on a Rigaku SCX Mini CCD diffractometer using a graphite-monochromatized MoK $\alpha$  radiation ( $\lambda = 0.071073$  nm) at 293(2) K. A

total of 17100 reflections were collected in the range of  $3.1^\circ \leq \theta \leq 25.1^\circ$  by using an  $\omega$ - $2\theta$  scan mode, of which 7463 were unique with  $R_{\text{int}} = 0.081$ . 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<sup>23,24</sup>. Positional parameters of all the H atoms for the carbon atoms were calculated geometrically and were allowed to ride on their respective parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ . All of the non-hydrogen atoms were refined by full-matrix least-squares techniques for 7439 observed reflections with  $I > 2\sigma(I)$  to give the final  $R = 0.0683$ ,  $wR = 0.1461$  ( $w = 1/[\sigma^2(F_o^2) + (0.0476P)^2]$ , where  $P = (F_o^2 + 2F_c^2)/3$ ,  $S = 1.01$ ). The highest peak and deepest hole in the final difference fourier map are  $-200$  and  $-390 \text{ e}\cdot\text{nm}^{-3}$ , respectively. Crystal data and structure refinement for the title complex are listed in Table-1. CCDC: 681080

## RESULTS AND DISCUSSION

**Structural analysis:** An ORTEP drawing of the molecular structure of the  $[\text{CoL}_2]\cdot[\text{ClO}_4]_2\cdot[\text{H}_2\text{O}]$  complex **1** is shown in Fig. 1, together with the corresponding atomic numbering scheme. X-ray crystal structure analysis of complex **1** reveals that the crystallographic unit of the title complex are made up of one Co(II) cation, two 4'-(4-cyanophenyl)-2,2':6',2''-terpyridine(cptpy), two  $\text{ClO}_4^-$  anions and one water molecule. However, One of the  $\text{ClO}_4^-$  groups is disordered in two orientation with the site-occupancy factors 0.71 (2) and 0.29 (2). No specific interactions between cation and  $\text{ClO}_4^-$  anions are observed. The selected bond lengths and angles of this compound are listed in Table-2.

For the cationic complex **1** comprised of one cation and two ligands, which is almost the same with those of other *bis*(terpyridyl)-Co(II) complexes<sup>25</sup>. The tridentate  $\text{N}_3$ -cptpy ligand coordinates cobalt(II) atom in a *fac* fashion giving a

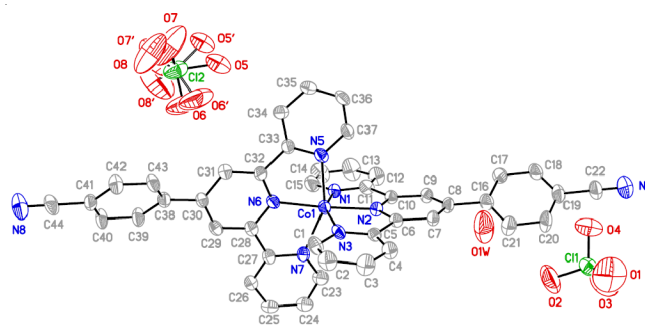


Fig. 1. A view of the title compound with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30 % probability level. Hydrogen atoms were omitted for clarity

tetragonally distorted  $[\text{CoN}_6]$  compressed octahedron geometry with all six coordination positions occupied by six N atoms belonging to two terpy units. The Co-N<sub>2</sub> and Co-N<sub>6</sub> bond distances of the central pyridine in the terpyridine unit [0.2001(6) and 0.2.010(6) nm, respectively] are obviously shorter than the Co-N<sub>1</sub>, N<sub>3</sub>, N<sub>5</sub> and N<sub>7</sub> bond distances of the side pyridine in the terpyridine unit [0.2110(6), 0.2126(6), 0.2150(5) and 0.2172(6) nm, respectively], which induced a pronounced distorted octahedral coordination geometry at the metal centre. The N<sub>2</sub>-Co1-N<sub>6</sub> angle, which involves the two Co-N central bonds, is  $172.6(2)^\circ$  and deviates from the ideal value of  $180^\circ$  for a normal octahedron. In addition, the remaining  $[\text{CoN}_6]$  angles also reflect the steric constraints imposed by the rigidity of the ligand (*i.e.*, the angles N<sub>1</sub>-Co1-N<sub>3</sub> ( $154.0(2)^\circ$ ) and N<sub>5</sub>-Co1-N<sub>7</sub> ( $154.35(19)^\circ$ ) are in the  $152$ - $165^\circ$  range). This is entirely typical of six-coordinate Co(II) complexes and is similar to the distortions observed in the (terpyridyl)-cobalt(II) complexes<sup>26</sup>. In addition, there is a clear relationship between the spin-state of the complex and the Co-N bond lengths according to the reported paper<sup>26,27</sup>. The differences in the average Co-N<sub>central</sub> or Co-N<sub>distal</sub> distances reflect the different

TABLE-1  
CRYSTAL DATA AND STRUCTURE REFINEMENT PARAMETERS FOR THE TITLE COMPLEX

Empirical formula	$\text{C}_{44}\text{H}_{30}\text{N}_8\text{O}_9\text{CoCl}_2$	F(000)	1932
Fw	944.59	Crystal size (mm)	$0.15 \times 0.10 \times 0.10$
T(K)	293	$\theta$ Range for data collection ( $^\circ$ )	$3.1$ - $25.1$
Crystal system	Monoclinic	Index ranges	$-16 \leq h \leq 16$ , $-14 \leq k \leq 14$ , $-30 \leq l \leq 30$
Space group	Cc	Reflections collected/unique	17100/7463 ( $R_{\text{int}} = 0.081$ )
a( $\text{\AA}$ )	14.018(12)	Refinement method	Full-matrix least-squares on $F^2$
b( $\text{\AA}$ )	12.223(10)	Data/restraints/parameters	7463/2/590
c( $\text{\AA}$ )	25.20(2)	Goodness-of-fit on $F^2$	1.01
$\beta$ ( $^\circ$ )	100.676(9)	R1 (on F) [ $I > 2\sigma(I)$ ]	0.0683
z	4	wR2 (on $F^2$ )	0.1461
$\rho$ (calc) ( $\text{g}/\text{cm}^3$ )	1.479	Largest diff. peak and hole [ $\text{e}\ \text{\AA}^{-3}$ ]	$-0.20$ and $0.39$
$\mu$ [ $\text{mm}^{-1}$ ]	0.598	Absorption correction	Multi-scan

TABLE-2  
SELECTED BOND LENGTHS (NM) AND BOND ANGLES ( $^\circ$ ) FOR THE TITLE COMPLEX

Bond	Distance (nm)	Bond	Distance (nm)	Angle ( $^\circ$ )	Angle ( $^\circ$ )	Angle ( $^\circ$ )	Angle ( $^\circ$ )
Co1-N1	0.2108(6)	Co1-N6	0.2009(6)	N5-Co1-N7	154.27(19)	N2-Co1-N3	77.6(2)
Co1-N2	0.2002(6)	Co1-N7	0.2171(6)	N2-Co1-N6	172.7(2)	N6-Co1-N3	98.4(2)
Co1-N3	0.2124(6)	C6-N2	0.1355(7)	N1-Co1-N3	154.0(2)	N6-Co1-N1	107.3(2)
Co1-N5	0.2151(6)	C10-N2	0.1357(7)	N2-Co1-N1	77.2(2)	N1-Co1-N7	89.3(2)
N1-C15	0.1350(9)	C5-N3	0.1355(7)	N3-Co1-N7	93.1(2)	N3-Co1-N5	93.2(2)
N1-C11	0.1358(8)	C1-N3	0.1340(8)	N1-Co1-N5	95.8(2)	N6-Co1-N7	76.7(2)
C44-N8	0.1143(9)	C11-O1	0.1377(8)	N2-Co1-N7	109.3(2)	N2-Co1-N5	96.4(2)

spin states of Co(II)<sup>27</sup>. In the complex (I), the Co-N distances (Table-2) are significantly longer than those observed in low-spin (LS) Co(II) species [0.1873(11)-0.1971(13)<sup>28</sup> and 0.1849(6)-0.1956(6) nm<sup>27</sup>, which are comparable to those of high-spin (HS) Co(II) species [0.2018(2) - 0.2180(3) nm]<sup>29</sup> and thus the complex (I) should exhibit a characteristic feature of the HS state.

The three pyridyl rings are approximately coplanar, with interplanar angles of 2.38 (0.43)° (between ring N1/C11-C15 and the central pyridyl ring N2/C6-C10), 3.93 (0.40)° (between ring N3/C1-C5 and the central pyridyl ring N2/C6-C10), 5.52 (0.29)° (between ring N5/C33-C37 and the central pyridyl ring N6/C28-C32), 10.98(0.29)° (between ring N7/C23-C27 and the central pyridyl ring N6/C28-C32), respectively. While the two tridentate ctpy ligands are nearly perpendicular to one another in the same complex. The benzene rings of the ctpy ligands in each case are twisted significantly with respect to the terpyridyl units, the pendant substituted phenyl rings A(C16-C21) and B (C38-C43) are twisted away from coplanarity with the adjacent terpyridyl unit C(N2/C6-C10) and D (N6/C28-C32) and forms dihedral angles of 32.36 (0.33)° (A/C) and 31.76 (0.32)° (B/D), which are almost equivalent. The C-C and C-N bond lengths within the aromatic rings are normal. These bond lengths are also similar to those observed for other cobalt(II) polypyridyl complexes<sup>25,26</sup>. In addition, there are no evidence that was observed for the existence of intermolecular aromatic  $\pi$ - $\pi$  stacking interactions between the terpyridyl unit molecules in the crystal structure.

**IR spectroscopy:** The major interest of the IR spectra of the title compounds is the bands corresponding to the cyanide groups. The title compound shows one intense IR absorptions at 2225 cm<sup>-1</sup> which can be assigned to the antisymmetric stretch of the non-coordinating cyanide groups of 4'-(4-cyanophenyl)-2,2':6',2''-terpyridine. Three signals at 790, 731 and 622 cm<sup>-1</sup> can be observed, corresponding to the bending vibration of the pyridine ring.

## Conclusion

The Co complex was successfully synthesized and characterized by single-crystal X-ray diffraction. The compounds crystallized in the space group of space group Cc. The Co(II) ion was six-coordinated by two tridentate 4'-(4-cyanophenyl)-2,2':6',2''-terpyridine ligand and form a distorted octahedral-pyramidal geometry.

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