Crystal Structure Determination of a new $[CoCl_2(phend)_2]$Complex

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Abstract

A novel Co(II) complex of phenanthridine (phend) ligand, *C*obalt(II) Dichlorophenanthridine , $[CoCl_2(phend)_2]$ has been synthesized from the reaction of $CoCl_2$ with phend, and their structures were studied by the single-crystal X-ray diffraction method. $[CoCl_2(phend)_2]$ crystallizes in the space group *P*21/*c* of the monoclinic system with *a* = 9.8653 (16) Å , *b* = 16.939(2) Å, *c* = 13.5957(18) Å and Z = 4. There are two molecules of the complex in the asymmetric units and in both molecules, the geometry around Cobalt(II) centers is distorted tetrahedral, formed by two nitrogen atom of two phend ligands and two chloride ions.

Keywords: Cobalt (II) -Phenanthridine -Crystal structure -tetrahedral.

1 Introduction

Phenanthridines are an important class of compounds because of their wide occurrence in natural products [1] as well as a broad spectrum of biological activities and unusual pharmacological utility that make them suitable for antineoplastic application. The high charge mobility of this planar heterocyclic system provides effective photoconducting and photovoltaic properties, required in the field of electroluminescence and dye lasers [2]. Phenanthridine (phend) and its derivatives have also been demonstrated to possess anti-tumor, antiviral, and cytotoxic activities as well as optoelectronic properties.

Significant number of biological interesting cobalt complexes exhibiting noteworthy in vitro antibacterial, antifungal, antioxidant, antiproliferative [3] and antiviral activity has been reported. Antibacterial is an agent that either kills bacteria or inhibits their growth [4].

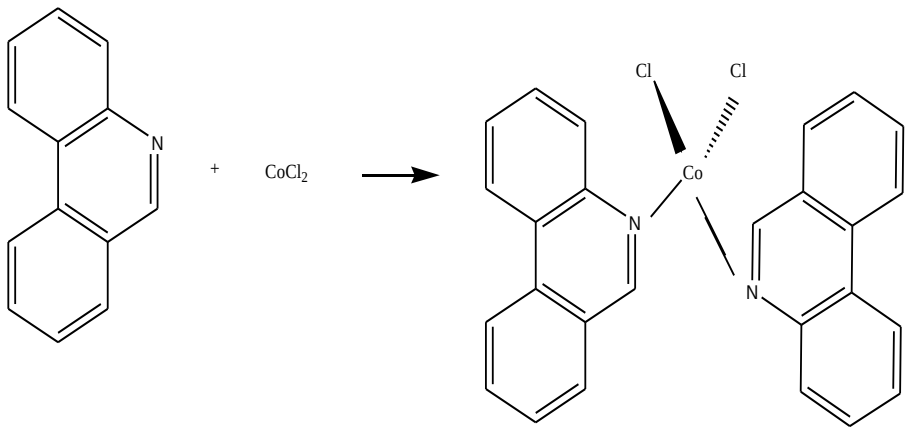
1.1 Background

Background: The presence of cobalt in the active center of vitamin B_{12}, which participates indirectly in the regulation of the DNA synthesis, is its most important role in vivo [5]. Additionally, a supplement of vitamin B_{12} contains cobalt and few cobalt-dependent proteins exist [5]. The biological relevance of cobalt compounds was initially reported sixty years ago [6].

Results and discussion

Synthesis of compound $[CoCl_2(phend)_2]$ was obtained by the reaction of one equivalent of $[CoCl_2.6H_2O]$, with two equivalent of phenanthridine in a mixture of C_2H_5OH at 40 °C after 30 min. The products were isolated in about 41 % yield. The synthetic routes of this complex is shown in Scheme 1.

Scheme 1 .



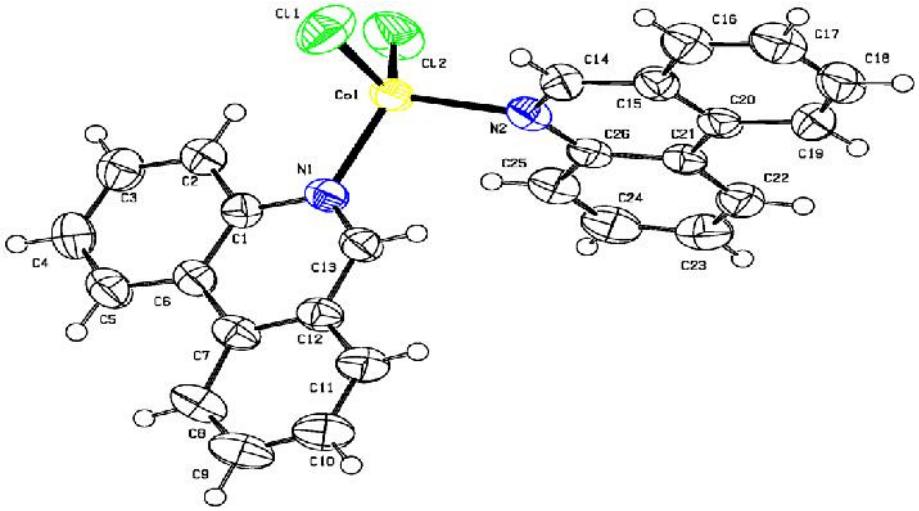


Fig. 1. ORTEP view of $[CoCl_2(phend)_2]$ with the atom numbering scheme.

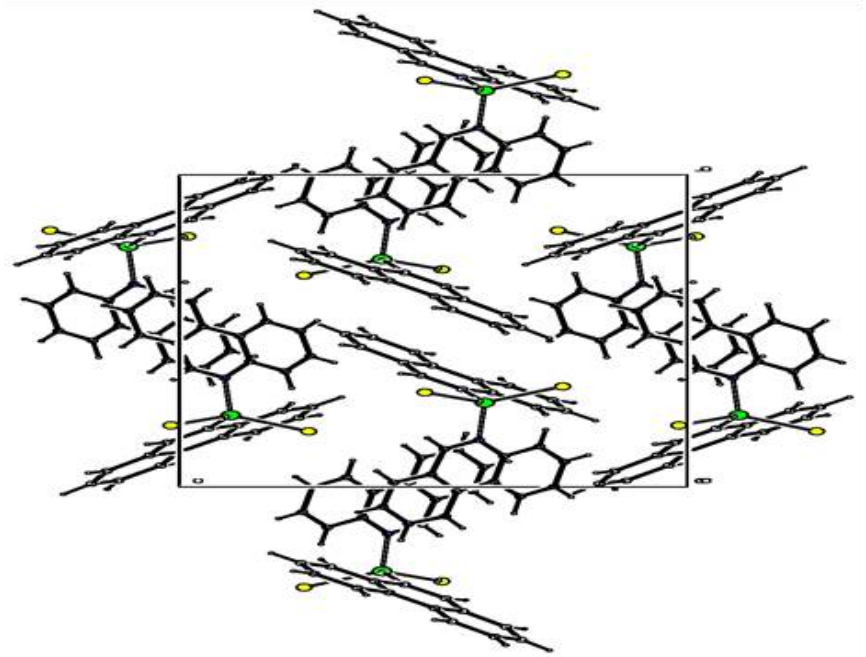


Fig. 2 . Crystal packing diagram of $[CoCl_2(phend)_2]$

Table. 1. Crystallographic and structure refinement data for $[CoCl_2(phend)_2]$ complex

Empirical formula	$C_{26}H_{18}Cl_2CoN_2$
Formula weight	488.25
Temperature	298 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
space group, Z	$P2_1/c$, 4
Unit cell dimensions	$a = 9.8653(16)$ Å $\alpha = 90^\circ$ $b = 16.939(18)$ Å $\beta = 105.471(12)^\circ$ $c = 13.5957(3)$ Å $\gamma = 90^\circ$
Volume	2189.6 (5) $Å^3$
Calculated density	1.481 mg/m^3
Absorption coefficient	1.044 mm^{-1}
F(000)	996
Crystal size mm^3	0.25 × 0.20 × 0.18
θ range for data collection	1.96° to 26.00°
Limiting indices	-12<=h<=12, -20<=k<=20, -16<=l<=16
Reflections collected / unique	118351 . 2280 [R(int) = 0.0808]
Completeness to θ = 27/00	100 %
Max. and min. transmission	0.8654 and 0.1521
Refinement method	Full-matrix least-squares on F^2
Final R indices [I>2sigma(I)]	R1 = 0.0378, wR2 = 0.0747
R indices (all data)	R1 = 0.0928, wR2 = 0.1034

Table. 2. Selected bond distances/Å for $[CoCl_2(phend)_2]$ complex

Co(1)-Cl(1)	2.2321(14)
Co(1)-Cl(2)	2.3309(13)
Co(1)-N(1)	2.044(3)
Co(1)-N(2)	2.064(3)

Description of the molecular structure of [$CoCl_2(phend)_2$] complex:

The molecular structure of [$CoCl_2(phend)_2$] complex with atom numbering scheme is shown in Fig. 1, while the crystal packing diagram is illustrated in Fig. 2. The X-ray crystallographic data are presented in Table 1. Selected bond lengths in Table 2 and Selected torsion angles in Table 3 and Selected bond angles are presented in Table 4.

The crystal structure of [$CoCl_2(phend)_2$] complex shows the presence of four molecules of the complex in the asymmetric unit (Fig. 2) which are identical. Analogous bond lengths and angles in the two molecules show only differences within few standard deviations. In both molecules, the geometry at the Cobalt(II) centers is distored tetrahedral arrangement typically seen for d^7 metal complexes, formed by two chloride ions and two nitrogen atom of two phenanthridine ligand. The lengths of Co(1)-N(1) (2.044(3) Å) and Co(1)-N(2) (2.064(3) Å) are not significantly different from each other (average: 2.054(3) Å) .

Table. 3. Selected torsion angles/° [$CoCl_2(phend)_2$]

C(2)C(1)N(1)Co(1)	6.6(5)	C(1)N(1)Co(1)Cl(2)	-41.7(3)
C(6)C(1)N(1)Co(1)	-172.7(3)	C(13)N(1)Co(1)Cl(1)	-86.9(3)
C(15)C(14)N(2)Co(1)	1.1(5)	C(1)N(1)Co(1)Cl(1)	84.6(3)
C(15)C(14)N(2)Co(1)	-172.7(3)	C(14)N(2)Co(1)N(1)	-116.5(3)
C(25)C(26)N(2)Co(1)	-5.9(5)	C(26)N(2)Co(1)N(1)	-69.9(3)
C(21)C(26)N(2)Co(1)	174.3(2)	C(14)N(2)Co(1)Cl(2)	-117.0(3)
C(13)N(1)Co(1)N(2)	27.7(30	C(26)N(2)Co(1)Cl(2)	-56.6(30)
C(1)N(1)Co(1)N(2)	-160.8(3)	C(14)N(2)Co(1)Cl(1	-5.9(3)
C(13)N(1)Co(1)Cl(2)	146.8(3)	C(26)N(2)Co(1)Cl(1)	-179.5(3)

Table. 4. Selected bond angles/° [$CoCl_2(phend)_2$]

C13-N(1)-Co(1)	117.2(2)	N(1)-CO(1)-Cl(2)	117.99(10)
C(1)-N(1)-Co(1)	123.6(2)	N(2)-CO(1)-Cl(2)	106.21(10)
C(14)-N(2)-Co(1)	118.4(3)	N(1)-CO(1)-Cl(1)	103.15(10)
C(26)-N(2)-Co(1)	122.6(3)	N(2)-CO(1)-Cl(1)	108.97(10)
N(1)-CO(1)-N(2)	106.21(10)	Cl(2)-CO(1)-Cl(1)	113.70(6)

Table. 5. π–π interaction for [$CoCl_2(phend)_2$] complex

Cg(i)-Cg(i)	**Cg-Cg distance(Å)**	**Symmetry code**
Cg(1)-Cg(4)	3.618(3)	2-X, 1-Y, 2-Z
Cg(1)-Cg(3)	3.618(3)	2-X, 1-Y, 2-Z
Cg(1)-Cg(2)	3.745(2)	1-x, -Y, 2-Z
Cg(1)-Cg(5)	3.679(3)	1-x, -Y, 2-Z
Cg(2)-Cg(5)	3.745(2)	1-X, -Y, 2-Z

Cg(I) denotes rings:

Cg(1)= N(2)-C(14)-C(15)-C(20)-C(21)-C(26) ,

Cg(2)= C(1)-C(2)-C(3)-C(4)-C(5)-C(6) ,

Cg(3)= C(7)-C(8)-C(9)-C(10)-C(11)-C(12) ,

Cg(4)= C(15)-C(16)-C(17)-C(18)-C(19)-C(20)

Cg(5)= C(21)-C(22)-C(23)-C(24)-C(25)-C(26)

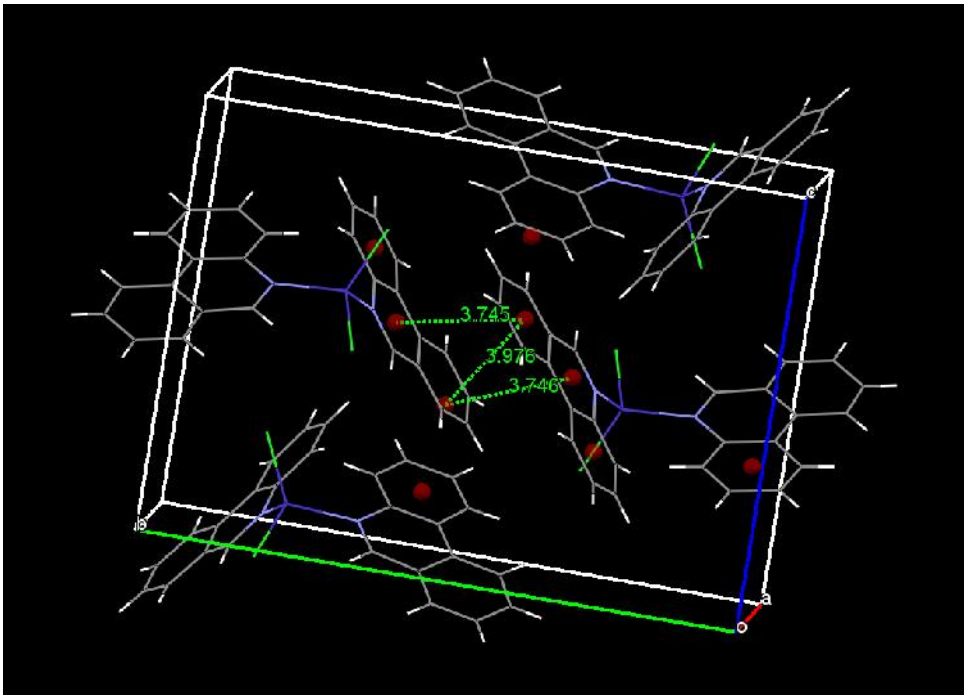


Fig. 3. π–π interaction for [$CoCl_2(phend)_2$]complex

Synthesis of Co (II) dichlorophenanthridine ($CoCl_2(phend)_2$)

A solution of 0.1 g phenanthridine (0.54 mmol) in 20 cm3 MeOH was added to a solution of 0.05 g [$CoCl_2.6H_2O$] (0.27 mmol) and the resulting blue solution was stirred for 30 min at 45°C. Then, it was left to evaporate slowly at room temperature. After 3 week, blue crystals were isolated. Yield (41 %).

Crystal structure determination and refinement

The X-ray diffraction measurements for compound was made on a STOE X-AREA area detector diffractometer with graphite monochromated Mo-Ka radiation (λ = 0.71073 **Å**) at 298 K. For data collection, blue crystals with dimensions of 0.22 × 0.17 × 0.80 **Å** were used for compound. The structures have been solved by direct methods and refined by full-matrix least-squares techniques on *F*2, using SHELXTL. The data were collected in the range1.96° <= θ <=

26.00°, -12<=h<=12, -20<=k<=20, -16<=l<=16. Multiscan absorption correction was applied using SADABS program [6]. Some software including Bruker SMART [7] and Stoe X-AREA [8] (data collection and cell refinement), Bruker SHELXTL [9], and Stoe X-AREA [8] (data reduction), and WinGX (publication material) [10] were properly used. The molecular graphics programs were ORTEP-3 for windows [11], DIAMIND 3.2, and PLATON.

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