

Structure of Chloro bis(1,10-phenanthroline)Cobalt(II) Complex, [Co(phen)₂(Cl)(H₂O)]Cl · 2H₂O

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Structure of Chloro bis(1,10-phenanthroline)Cobalt(II) Complex, [Co(phen)₂(Cl)(H₂O)]Cl · 2H₂O

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요약. [Co(phen)₂(Cl)(H₂O)]Cl · 2H₂O(phen=1,10-phenanthroline)의 결정구조는 X-ray에 의하여 결정되었다. 그 결정은 $a=9.662(2)$, $b=11.445(1)$, $c=13.037(2)$ Å, $\alpha=64.02(1)$, $\beta=86.364(9)$, $\gamma=78.58(2)^\circ$ 그리고 $Z=2$ 의 격자인자를 갖는 triclinic계와 space group이 P1의 구조로 결정화 되었다. 배위된 양이온은 두개의 Phen 리간드, 하나의 chloride이온과 하나의 H₂O 리간드가 cis 배열로 킬레이트된 6배위 코발트 원자가 포함된다. 코발트에 배위된 chloride에 대해서, 결정구조를 이루는 하나의 chloride이온과 네개의 물분자가 있다. 고체상태에서, 제목의 화합물은 수소결합을 통하여 3차원 그물구조를 갖는다.

주제어: 코발트 착화합물, 1,10-Phenanthroline, 수소결합, 그물구조

ABSTRACT. The crystal structure of [Co(phen)₂(Cl)(H₂O)]Cl · 2H₂O(phen=1,10-phenanthroline) has been determined by X-ray crystallography. It crystallizes in the triclinic system, space group P₁, with lattice parameters $a=9.662(2)$, $b=11.445(1)$, $c=13.037(2)$ Å, $\alpha=64.02(1)$, $\beta=86.364(9)$, $\gamma=78.58(2)^\circ$, and $Z=2$. The coordinated cations contain a six-coordinated cobalt atom chelated by two phen ligands and one chloride anion and one water ligand in *cis* arrangement. In addition to the chloride coordinated to the cobalt, there are one chloride ion and four water molecules which complete the crystal structure. In the solid state, the title compound forms three dimensional network structure through hydrogen bonds, within which exists the strongest hydrogen bond (O(3)-O(4)-2.33Å). The intermolecular hydrogen bonds connect the [Co(phen)₂(Cl)(H₂O)]⁺, H₂O moieties and chloride ion.

Keywords: Cobalt Complexes, 1,10-Phenanthroline Ligands, Hydrogen Bonds, Network

INTRODUCTION

Metal complexes of the type [M(LL)₃]ⁿ⁺, where LL is either 1,10-phenanthroline (phen) or a modified phen ligand, are particularly attractive species

for developing new diagnostic and therapeutic agents that can recognize and cleave DNA.^{1,2} The ligands or the metal in these complexes can be varied in an easily controlled manner to facilitate an individual application, thus providing an easy access

for the understanding of details involved in DNA-bonding and cleavage.³ Some [Co(phen)₂XY]⁺ complexes have the DNA-binding and photochemical DNA cleavage characteristics.⁴ Cobalt complexes with phen, halogen ions and H₂O ligands have also been studied in connection with the mechanism of irreversible autoxidation reactions,⁵⁻⁸ subsequent *cis-trans* isomerization^{9,11} and equilibrium in solution at different pH values.¹²⁻¹³ To our knowledge, there are a little crystal structure of Co(II) with phen ligands forming coordinating complexes which have been reported so far because of Co(II) instability. In this paper, we describe the crystal structure of chloro bis(1,10-phenanthroline) cobalt(II) complex, [Co(phen)₂(Cl)(H₂O)] Cl · 2H₂O.

EXPERIMENT SECTION

Preparation of [Co(phen)₂(Cl)(H₂O)] Cl · 2H₂O.

The reagents CoCl₂·6H₂O (A.R.), and phen (A.R.) were commercially available. To a warm solution of phen (2.97 g, 15 mmol) in EtOH (50 mL) was added with string [CoCl₂ · 6H₂O] (1.19 g, 5 mmol) and the mixture were refluxed for 20 mins. The red solution was filtered and the filtrate was left to stand undisturbed. Upon slow evaporation at room temperature, a red crystalline solid appeared several weeks later and was separated by filtration. The C, H and N contents were determined by elemental analysis. [Found: C, 51.83; H, 4.70; N, 22.00%. Calcd. C, 51.84; H, 4.62; N, 22.67%].

X-ray structure determination. The selected crystal of [Co(phen)₂(Cl)(H₂O)] Cl · 2H₂O was mounted on an Siemens P4 diffractometer. Reflection data were measured at 293K, using graphite mono-chromated Mo K α ($\lambda=0.71073$ Å) radiation ω -2 θ scan mode. Intensities were corrected for Lorentz and polarization effects and empirical absorption, and the data reduction using SHELXTL5.¹⁴ The structure were solved by direct methods using SHELXS86.¹⁵ All the nonhydrogen atoms were refined on F^2 anistropically by full-matrix least squares method.¹⁶ All the hydrogen atoms were placed in calculated positions assigned fixed isotropic thermal parameters at 1.2 times the equiva-

Table 1. Summary of Crystallographic Results for [Co(phen)₂(Cl)(H₂O)] Cl · 2H₂O

| Color shape | Red:prism |
|--|---|
| Empirical formula | C ₂₁ H ₁₂ Cl ₂ CoN ₆ O ₃ |
| Formula weight | 544.29 |
| Crystal size (nm) | 0.80 0.60 0.60 |
| Space group | <i>P</i> $\bar{1}$ |
| Unit cell dimensions | |
| <i>a</i> , Å | 9.662(2) |
| <i>b</i> , Å | 11.445(1) |
| <i>c</i> , Å | 13.037(2) |
| α , | 64.02(1) |
| β , | 86.364(9) |
| γ , | 78.58(2) |
| Cell volume, Å ³ | 1269.9(4) |
| <i>Z</i> | 2 |
| <i>D</i> (calcd.) Mg m ⁻³ | 1.423 |
| Abs coeff. mm ⁻¹ | 0.918 |
| <i>F</i> (000) | 558 |
| Radiation | Mo K α ($\lambda=0.71073$ Å) |
| Temp. K | 293(2) |
| θ range, ° | 2.01 to 25.00 |
| Limiting indices | -1 \leq h \leq 11, -12 \leq k \leq 12, -15 \leq l \leq 15 |
| Reflections collected | 5207 |
| Independent reflections | 4349 [<i>R</i> _{min} = 0.0747] |
| Tmax. and Tmin. | 0.4431, 0.3972 |
| <i>R</i> [<i>I</i> > 2 σ (<i>I</i>)] | <i>R</i> 1=0.077, w <i>R</i> 2=0.1947 |
| <i>R</i> (all data) | <i>R</i> 1=0.0833, w <i>R</i> 2=0.1968 |
| Goodness-of-fit on <i>F</i> ² | 1.298 |
| Largest diff. peak and hole | 1.659 and -1.192 eÅ ⁻³ |

lent isotropic *U* of the atoms to which they are attached and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in structure-factor calculations. The final least-square cycle gave *R*=0.0747, *R*_w=0.0919 for 3639 reflections with *I*>2 σ (*I*); the weighting scheme, $w=1/[\sigma^2(F_o^2)+(0.1247P)^2+0.0000P]$, where $P=(F_o^2+2F_c^2)/3$. Atomic scattering factors and anomalous dispersion corrections were taken from *International Table for X-Ray Crystallography*.¹⁷ A summary of the key crystallographic information is given in Table 1. The final position parameters of nonhydrogen atoms are given in Table 2. Selected bond lengths (Å), possible hydrogen bonds (Å) and bond angles (°) are presented in Table 3, respectively.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \cdot 10^3$). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

| | x | y | z | U_{eq} |
|-------|----------|-----------|----------|-----------------|
| Co(1) | 2011(1) | -1326(1) | 7779(1) | 30(1) |
| Cl(1) | 747(1) | 452(1) | 6149(1) | 42(1) |
| O(1W) | 414(4) | -990(3) | 8850(3) | 41(1) |
| N(1) | 2900(4) | -3066(4) | 9317(3) | 34(1) |
| N(2) | 1177(4) | -2859(3) | 7669(3) | 34(1) |
| N(3) | 3848(4) | -1595(3) | 6829(3) | 32(1) |
| N(4) | 3308(4) | -140(4) | 8008(3) | 37(1) |
| C(1) | 3726(6) | -3160(5) | 10108(4) | 46(1) |
| C(2) | 4151(7) | -4328(6) | 11097(5) | 62(2) |
| C(3) | 3637(7) | -5428(6) | 11264(5) | 60(2) |
| C(4) | 2740(6) | -5372(5) | 10437(4) | 46(1) |
| C(5) | 2400(5) | -4169(4) | 9469(4) | 35(1) |
| C(6) | 1491(5) | -4060(4) | 8588(4) | 34(1) |
| C(7) | 967(6) | -5172(5) | 8704(5) | 46(1) |
| C(8) | 117(6) | -5012(6) | 7825(6) | 58(2) |
| C(9) | -189(7) | -3805(6) | 6876(5) | 60(2) |
| C(10) | 367(6) | -2749(5) | 6842(4) | 45(1) |
| C(11) | 2169(7) | -6479(5) | 10514(5) | 62(2) |
| C(12) | 1342(7) | -6378(5) | 9700(6) | 59(2) |
| C(13) | 4082(5) | -2275(5) | 6223(4) | 41(1) |
| C(14) | 5323(6) | -2356(5) | 5619(4) | 47(1) |
| C(15) | 6351(5) | -1694(5) | 5646(4) | 44(1) |
| C(16) | 6136(5) | -965(4) | 6285(4) | 38(1) |
| C(17) | 4860(5) | -944(4) | 6862(4) | 33(1) |
| C(18) | 4573(5) | -176(4) | 7502(4) | 35(1) |
| C(19) | 5604(5) | 498(5) | 7582(4) | 43(1) |
| C(20) | 5256(7) | 1256(6) | 8208(5) | 64(2) |
| C(21) | 3982(7) | 1302(7) | 8705(6) | 69(2) |
| C(22) | 3032(6) | 578(5) | 8599(5) | 52(1) |
| C(23) | 7148(5) | -261(5) | 6373(4) | 48(1) |
| C(24) | 6905(6) | 424(6) | 7007(5) | 51(1) |
| Cl(2) | 1161(2) | -1804(1) | 11371(1) | 52(1) |
| O(2W) | -80(21) | -6895(7) | 6225(7) | 204(10) |
| O(3W) | 2187(19) | -5560(18) | 5335(13) | 192(8) |
| O(5W) | 3892(21) | -5290(12) | 6470(13) | 167(7) |
| O(4W) | 6693(33) | -5888(19) | 6198(22) | 328(17) |

RESULT AND DISCUSSION

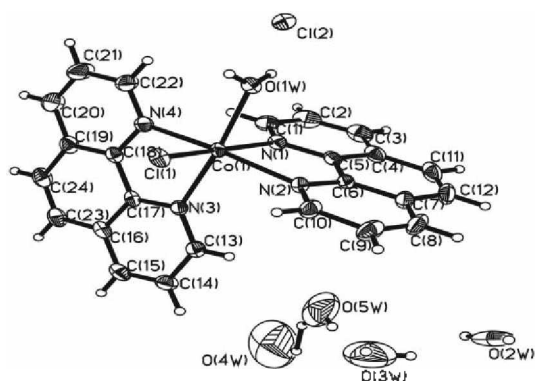
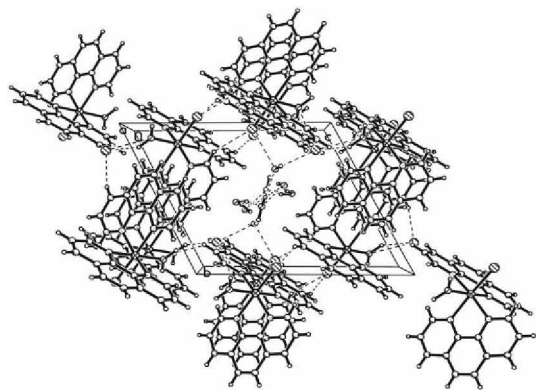
Structure. The X-ray structure of the complex $[\text{Co}(\text{phen})_2(\text{Cl})(\text{H}_2\text{O})]\text{Cl} \cdot 2\text{H}_2\text{O}$ consists of the $[\text{Co}(\text{phen})_2(\text{Cl})(\text{H}_2\text{O})]$ molecules and one Cl^- ion and four molecules of water. Fig. 1 shows a perspective view of the title compound with atomic numbering scheme, and Fig. 2 a perspective view of the crys-

tal packing in the unit cell.

The title compound contains a six-coordinated cobalt atom chelated by two phen ligands and one Cl^- anion and one H_2O molecules in a *cis* arrangement with the angles $\text{O}(1\text{w})-\text{Co}(1)-\text{N}(2)=93.95(13)^\circ$ and $\text{O}(1\text{w})-\text{Co}(1)-\text{N}(3)=171.29(13)^\circ$, $\text{Cl}(1)-\text{Co}(1)-\text{N}(2)=96.29(10)^\circ$ and $\text{Cl}(1)-\text{Co}(1)-\text{N}(1)=172.05(12)^\circ$, $\text{O}(1\text{w})-\text{Co}(1)-\text{Cl}(1)=171.29(13)^\circ$. The angles of the title compound in the coordination sphere differ

Table 3. Selected bond lengths (Å) and bond angles ($^\circ$) of the title compound

| | | | |
|-------------------|----------|------------------|----------|
| Co(1)-O(1W) | 2.107(3) | Co(1)-N(2) | 2.132(4) |
| Co(1)-N(4) | 2.139(4) | Co(1)-N(3) | 2.149(4) |
| Co(1)-N(1) | 2.183(4) | Co(1)-Cl(1) | 2.389(1) |
| N(1)-C(1) | 1.297(6) | N(1)-C(5) | 1.370(6) |
| N(2)-C(10) | 1.320(6) | N(2)-C(6) | 1.361(5) |
| O(2w)-O(3w) | 3.07(1) | O(2w)-O(4w) | 3.10(3) |
| O(3w)-O(4w) | 2.33(3) | O(4w)-O(5w) | 3.17(3) |
| Cl(1)-O(2w) | 3.027(9) | Cl(2)-O(1w) | 3.154(4) |
| Cl(2)-O(2w) | 3.04(1) | | |
| O(1W)-Co(1)-N(2) | 94.00(1) | O(1W)-Co(1)-N(4) | 94.5(1) |
| N(2)-Co(1)-N(4) | 166.1(2) | O(1W)-Co(1)-N(3) | 171.3(1) |
| N(2)-Co(1)-N(3) | 93.3(1) | N(4)-Co(1)-N(3) | 77.5(1) |
| O(1W)-Co(1)-N(1) | 85.2(1) | N(2)-Co(1)-N(1) | 77.5(1) |
| N(4)-Co(1)-N(1) | 92.3(2) | N(3)-Co(1)-N(1) | 91.6(1) |
| O(1W)-Co(1)-Cl(1) | 90.3(1) | N(2)-Co(1)-Cl(1) | 96.3(1) |
| N(4)-Co(1)-Cl(1) | 94.7(1) | N(3)-Co(1)-Cl(1) | 93.7(1) |
| N(1)-Co(1)-Cl(1) | 172.1(1) | C(1)-N(1)-Co(1) | 129.4(3) |

Fig. 1. Molecular structure for $[\text{Co}(\text{phen})_2(\text{Cl})(\text{H}_2\text{O})] \cdot \text{Cl} \cdot 2\text{H}_2\text{O}$ with the atomic numbering scheme.Fig. 2. A view of the crystal packing down the a axis for $[\text{Co}(\text{phen})_2(\text{Cl})(\text{H}_2\text{O})] \cdot \text{Cl} \cdot 2\text{H}_2\text{O}$.

from the ideal 90° . This distortion can be rationalized after considering the restriction imposed by the ligands. The bite angles between the phen chelate rings and cobalt atom are the same ($77.5(1)^\circ$) which is lower than that of $[\text{Co}(\text{phen})_2(\text{H}_2\text{O})_2](\text{NO}_3) \cdot 2\text{H}_2\text{O}$,¹⁸ $[\text{Co}(\text{phen})_2(\text{Cl})(\text{H}_2\text{O})]^{2+}$,¹⁹ and $[\text{Co}(\text{phen})_2\text{Cl}_2]\text{Cl} \cdot 3\text{H}_2\text{O}$.²⁰ This can be interpreted in terms of the rigidity of phen ligands and the difference of valence state of cobalt. The two phen ligands are bidentately bonded to cobalt, forming five-member chelate rings. The Co-N bond distances are shorter than the Co-N bond distances found in other Co^{2+} with N atom coordinated complexes²¹⁻²² and longer than those found in Co^{3+} coordinated complexes.²³⁻²⁵ The bond distances of Co-N(1) and Co-N(3) which are *trans* to the Cl and H_2O are slightly longer than those of Co-N(2) and Co-N(4) which are *cis* to the Cl and H_2O . The longest bond distance is Co-N(3), which can be interpreted on the basis of the repulsion effect of Cl⁻ ion having bigger volume than O atom. The bond distances of C-N and C-C in the title compound all fall within the range of the literature values.²⁶ The two aromatic ring systems in each phen are coplanar under the experimental error. The dihedral angles between the two phen ligands is 84.1° . The four lattice water molecules [O(2), O(3), O(4) and O(5)] form hydrogen bonded to each other

and O(3) with O(4) form the strongest hydrogen bond. The O(3)-O(4) distance is 2.33 Å, which is 0.43 Å and 0.50 Å, shorter than that of ice (2.76 Å) and pure water (2.83 Å), respectively.²⁷⁻²⁸ The guest Cl⁻ ion with coordinated water forms hydrogen bond connecting two [Co(phen)₂(Cl)(H₂O)]⁺ molecules. The coordinated Cl atom with guest water forms hydrogen bond. In the solid state, the intermolecular hydrogen bonds connect the [Co(phen)₂(Cl)(H₂O)]⁺, H₂O moieties and chloride ion and make the title compound form three dimensional network structure.

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