

2'-(2-噻吩亚甲基)-2-羟基苯甲酰肼钴(III) 配合物的合成、表征及晶体结构

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Synthesis, Characterization and Crystal Structure of Cobalt(III) Complex with 2'-(2-Thienylidene)-2-Hydroxybenzoylhydrazide

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Abstract: In ethanol, a mononuclear cobalt(II) complex incorporating 2'-(2-Thienylidene)-2-Hydroxybenzoylhydrazide has been synthesized and characterized by IR, UV-Vis, elemental analysis and X-ray crystal structure analysis. The crystal belongs to triclinic system, space group $P\bar{1}$ with cell constant, $a=1.230\ 69(10)$ nm, $b=1.329\ 18(11)$ nm, $c=1.330\ 56(11)$ nm, $\alpha=113.702(2)^\circ$, $\beta=91.590(2)^\circ$, $\gamma=100.846(2)^\circ$, $V=1.944\ 4(3)$ nm³, $Z=2$, $\mu=0.662$ mm⁻¹, $D_c=1.482$ g·cm⁻³, $F(000)=896$, $R_{int}=0.048\ 7$. The crystal structure shows an anionic didentate ligand O and N donors in this work. The cobalt(III) atom is hexacoordinated with oxygen atom from keto group and nitrogen atom from amide to form a cobalt atom for the core octahedral structure. CCDC: 748882.

Key words: cobalt complexes; 2'-(2-thienylidene)-2-hydroxybenzoylhydrazide; crystal structure; synthesis

0 Introduction

Most Schiff base compounds with biological activity, pesticide, medicine and analysis of such areas has been widely used^[1-6], withal Schiff bases are useful chelators because of their preparative accessibilities, structural varieties and varied denticities^[7-9]. Recently, mono- and polynuclear complexes of pseudohalides like azides have been well established with strong covalent

bonds^[10,11]. Cobalt is important in the lives of organisms elements, many cobalt Schiff base complexes have been studied because of their interesting properties such as models for the vitamine B12 coenzyme^[12,13]. These properties were examined with the aim to gain an insight into the chemistry of the related biological molecules. We have reported Schiff base complexes and the structure^[14]. In order to study the structure of cobalt complexes and properties, herein we reported the title

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compound of the cobalt hexacoordinated structure.

1 Experimental

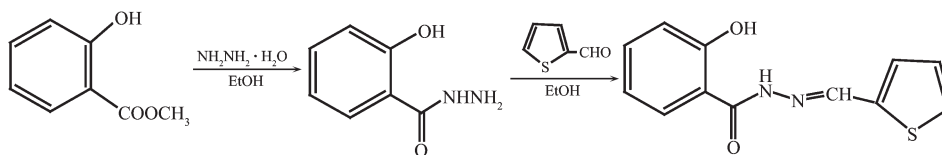
1.1 Reagent and apparatus

Chemicals were commercial reagents (A.R.) and used without further purification. Solvents were of analytical grade and dried and purified before use by the usual methods. Elemental analysis was performed on a Perkin-Elmer 2400/II instrument. IR spectra were recorded on a Nicolet FTIR 5700 spectrophotometer with KBr pellets in the range of 4 000~400 cm^{-1} . The UV-Vis measurements were carried out in DMF solution using a Shimadzu 2401PC UV-Vis spectrophotometer. ^1H NMR spectra were measured with a Varian XL200 nuclear magnetic resonance spectrometer using DMSO as solvent and TMS as internal

standard. The diffraction data were collected on a Bruker smart CCD 1000 diffractometer. The melting point was determined on a WZ-1 melting point apparatus and uncorrected.

1.2 Synthesis of 2'-(2-Thienylidene)-2-Hydroxybenzoylhydrazide

2-hydroxybenzoylhydrazine was dissolved in anhydrous ethanol and 2-thienyaldehyde was added. The mixture was refluxed for 2 h and washed with ethanol (Scheme 1). The product was recrystallized from ethanol and dried under reduced pressure to obtain the 2'-(2-Thienylidene)-2-Hydroxybenzoylhydrazide. m.p. 251 ~ 252 $^{\circ}\text{C}$. Yield: 85%. Anal. Calcd.: C 58.52; H 4.09; N 11.38. Found: C 58.44; H 3.94; N 11.27. UV-Vis (DMF) $\lambda_{\text{max}}/\text{nm}$, 245, 302. IR (KBr, cm^{-1}): 3 346 (m, $\nu(\text{N-H})$), 3 070(m, (O-H)), 1 653(m, $\nu(\text{C=O})$), 1 627(s, $\nu(\text{C=N})$).



Scheme 1 Reaction equation for the compound

1.3 Synthesis of cobalt complexes

[Co(C₁₂H₉N₂O₂S)₃](C₃H₇NO)

A mixture of Co(CH₃COO)₂·4H₂O (1 mmol, 0.25 g), 2'-(2-thienylidene)-2-hydroxybenzoylhydrazide 3 mmol and ethanol 25 mL was refluxed for 2 h. The brown precipitate was filtered off, washed with ethanol and dried over P₂O₅ for 24 h. The compound is soluble in a range of common organic solvents like DMF and pyridine but is insoluble in ethanol and water. The solid 0.10 g was dissolved in 5 mL DMF to give, with slow evaporation over 20 d at room temperature, brown block crystals adequate for X-ray analysis. Yield: 74%. Anal. Calcd for [Co(C₁₂H₉N₂O₂S)₃](C₃H₇NO): C 53.98; H 3.95; N 11.30; Found: C 53.91; H 3.88; N 11.34. UV-Vis (DMF) $\lambda_{\text{max}}/\text{nm}$, 269, 362. IR(KBr, cm^{-1}): 3 431(m, $\nu(\text{N-H})$), 3 056(m, (O-H)), 1 624(m, $\nu(\text{C=O})$), 1 570(s, $\nu(\text{C=N})$), 546(m, $\nu(\text{Co-O})$), 443(m, $\nu(\text{Ni-N})$)^[15].

1.4 Crystal structure determination

A brown single crystal with dimensions of 0.31 mm × 0.20 mm × 0.09 mm was put on Bruker Smart CCD 1000 diffractometer equipped with a graphite-monochromatic

Mo $K\alpha$ radiation ($\lambda=0.071\,073\,\text{nm}$) by using φ - ω scan mode at 293(2) K. Out of the total 11 174 reflections collected in the range of $1.68^{\circ} \leq \theta \leq 26.50^{\circ}$ ($-15 \leq h \leq 13$, $-8 \leq k \leq 16$, $-16 \leq l \leq 15$), 7 896 were independent with $R_{\text{int}}=0.048\,7$, of which 4 988 were considered to be observed ($I>2\sigma(I)$) and used in the succeeding refinement. The crystal structure was solved with direct method using SHELXS-97 program^[16]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located at theoretical position. The final refinement including hydrogen atoms converged to $R_1=0.062\,5$, $wR_2=0.138\,9$, $w=1/[(\sigma^2(F_o)^2+(0.066\,2P)^2)]$, where $P=(F_o^2+2F_c^2)/3$, $(\Delta/\sigma)_{\text{max}}=0.076$, $S=0.978$, $(\Delta\rho)_{\text{max}}=503\,\text{e}\cdot\text{nm}^{-3}$ and $(\Delta\rho)_{\text{min}}=-360\,\text{e}\cdot\text{nm}^{-3}$.

CCDC: 748882.

2 Results and discussion

2.1 UV-Vis and IR spectra

The IR spectrum of the ligand shows absorption bands at 1 653 cm^{-1} attributable to the $\nu(\text{C=O})$ stretching vibration is markedly shifted to lower energy at 1

603 cm^{-1} of complexes which indicates the coordination in the enolate form. A sharp band at 1 627 cm^{-1} in the spectrum of ligand is shifted to lower frequencies by 5 cm^{-1} in the spectra of the complexes which indicates coordination via the amide nitrogen. Moreover, the Co-O vibration is found at 546 cm^{-1} and the Co-N vibration is found at 443 cm^{-1} [15]. These peaks are in agreement with related complexes regardless of the degree of distortion of the coordination environment.

The electronic spectra were recorded in DMF solutions in the 200~400 nm range for the free ligand and the complexes. The band of 302 and 362 nm may be assigned to a $n-\pi^*$ transition of conjugation between lone-pair electron of p orbital of N atom in C=N group and a conjugated π bond of benzene ring. A peak at 245 and 269 nm is assigned to a $\pi-\pi^*$ transition of conjugation system of Schiff base[17]. The absorption spectra of complexes is compared with the ligand, the complexes exhibit reduced oscillator strengths and blue shifts versus ligand, this modification can be related to the molecular structure of the complexes, the planar geometry of the ligand is hampered by steric hindrance in complexes. The resulting lack of conjugation is consistent with the changes observed in the intensity

and energy of the charge transfer transition. The shift from characteristic band could explain that the title complexes were formed.

2.2 Crystal structure

The molecular structure of the intramolecular hydrogen bonds in Fig.1. The selected bond lengths and bond angles in Table 1. The hydrogen bond lengths and bond angles are given in Table 2.

The 2'-(2-thienylidene)-2-hydroxybenzoylhydrazide was used as an anionic didentate O and N donors

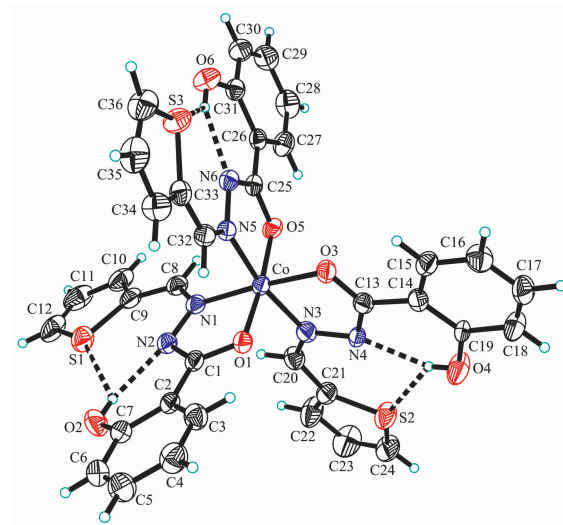


Fig.1 Hydrogen bond of the title compound

Table 1 Selected bond lengths (nm) and angles ($^{\circ}$) of title compound

Co-O(1)	0.186 9(3)	N(2)-C(1)	0.131 4(5)	O(1)-C(1)	0.129 3(4)
Co-O(5)	0.188 4(3)	N(3)-C(20)	0.126 9(5)	O(2)-C(7)	0.133 7(5)
Co-O(3)	0.189 4(3)	N(3)-N(4)	0.139 6(4)	O(3)-C(13)	0.126 4(4)
Co-N(5)	0.190 2(3)	N(4)-C(13)	0.131 9(4)	O(4)-C(19)	0.139 3(4)
Co-N(1)	0.191 3(3)	N(5)-C(32)	0.128 6(5)	O(5)-C(25)	0.128 3(4)
Co-N(3)	0.192 2(3)	N(5)-N(6)	0.137 4(4)	O(6)-C(31)	0.132 9(5)
N(1)-C(8)	0.128 8(5)	N(6)-C(25)	0.131 5(5)	O(7)-C(37)	0.106 7(11)
N(1)-N(2)	0.138 5(4)	N(7)-C(37)	0.124 3(8)		
O(1)-Co-O(5)	174.84(10)	O(3)-Co-N(3)	82.11(12)	C(32)-N(5)-Co	126.5(3)
O(1)-Co-O(3)	90.51(12)	N(5)-Co-N(3)	169.17(13)	N(6)-N(5)-Co	113.6(2)
O(5)-Co-O(3)	92.66(12)	N(1)-Co-N(3)	98.65(13)	C(1)-O(1)-Co	111.3(2)
O(1)-Co-N(5)	93.70(13)	C(8)-N(1)-N(2)	119.5(3)	C(13)-O(3)-Co	111.3(2)
O(5)-Co-N(5)	82.37(12)	C(8)-N(1)-Co	127.8(3)	C(25)-O(5)-Co	110.2(2)
O(3)-Co-N(5)	87.70(12)	N(2)-N(1)-Co	112.7(2)	O(1)-C(1)-N(2)	122.8(4)
O(3)-Co-N(1)	173.18(14)	C(1)-N(2)-N(1)	110.1(3)	O(1)-C(1)-C(2)	117.5(4)
N(5)-Co-N(1)	91.90(12)	C(20)-N(3)-N(4)	119.7(3)	O(1)-Co-N(1)	82.71(13)
O(1)-Co-N(3)	90.07(13)	C(20)-N(3)-Co	127.7(3)	O(5)-Co-N(1)	94.04(13)
O(5)-Co-N(3)	94.39(13)	N(4)-N(3)-Co	112.4(2)		

Table 2 Hydrogen bonds for title compound

D-H...A	d(D-H) / nm	d(H...A) / nm	d(D...A) / nm	∠(DHA) / (°)
O(2)-H(2A)...N(2)	0.82	1.94	2.655(5)	145.2
O(2)-H(2A)...S(1)	0.82	2.59	3.184(4)	130.9
O(4)-H(4A)...N(4)	0.82	1.94	2.655(4)	145.3
O(4)-H(4A)...S(2)	0.82	2.52	3.133(3)	132.9
O(6)-H(6A)...N(6)	0.82	1.92	2.646(4)	146.8
O(6)-H(6A)...S(3)	0.82	2.64	3.227(3)	129.8

ligand in this work. The hexacoordinate Co(III) is defined by the three keto oxygen atoms O1, O3 and O5, by the three amide nitrogen atoms N1, N3 and N5. The two oxygen atoms occupy the axial positions forming the octahedral coordination sphere. Three five-membered rings shaped by cobalt and ligands are defined by Co-O1-C1-N1-N2, Co-O5-C25-N6-N5 and Co-O3-C13-N4-N3, with the plane angles of 89.92 (0.08)° and 84.58 (0.10)°, respectively, showed that three plane almost perpendicular to each other. The angles O1-Co-O3, O3-Co-O5, O5-Co-N1 and N1-Co-O1 combined sum of 359.92°, indicated that the N1, O5, O3 and O1 atoms almost in the same plane, similarly N1, N3, N5, O3 and O1, O5, N3, N5 atoms almost the same plane. The bond distances Co-O are [0.186 9~0.189 4 nm] and Co-N [0.190 2~0.192 2 nm], which are comparable with analogous hexacoordinated cobalt complexes incorporating Schiff base ligands^[18], and appreciably longer than those of the square planar or tetrahedrally complexes^[19]. The Co-O bond lengths are slightly shorter than Co-N bond length indicates that the keto oxygen atoms coordinates slight strongly than the amide nitrogen atoms^[20].

In the title complex, the intramolecular hydrogen bonds could be also observed, the intramolecular hydrogen bonds O-H...N and O-H...S are generated and contribute to the formation of two six-membered rings of the ligands, these hydrogen bonds connect to the stability of compounds.

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