

双肟钴(II)配合物的合成及晶体结构

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摘要: 利用螯合双肟配体 $H_2L(H_2L=4,4'$ -二硝基-2,2'-[1,2-亚乙基二氧双(氮次甲基)]二酚)合成了 1 个三核钴(II)配合物 $[Co_3(OAc)_2(CH_3OH)_2L_2] \cdot 2CH_3CN$, 并用 X-射线单晶衍射分析确定了其晶体结构。配合物晶体属三斜晶系, $P\bar{1}$ 空间群, 由 3 个 Co(II)离子、2 个四齿的 L^{2-} 单元、2 个配位的乙酸根、2 个配位的甲醇分子和 2 个结晶的无序乙腈分子组成, 其几何构型为稍微扭曲的八面体, 且配合物通过分子间 $C-H \cdots O$ 氢键形成了 1 种二维超分子结构。

关键词: 双肟配体; 钴(II)配合物; 合成; 晶体结构

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Synthesis and Crystal Structure of a Bisoxime Cobalt(II) Complex

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Abstract: A trinuclear Co(II) complex, $[Co_3(OAc)_2(CH_3OH)_2L_2] \cdot 2CH_3CN$, was synthesized with Salen-type bisoxime ligand 4,4'-dinitro-2,2'-[1,2-ethylenedioxybis(nitrilomethylidyne)]diphenol (H_2L), and characterized by elemental analyses, IR spectra and X-ray diffraction method. X-ray single crystal structure analysis reveals that the complex crystallizes in the triclinic system, space group $P\bar{1}$ with cell parameters: $a=0.992\ 80(8)$ nm, $b=1.084\ 4(1)$ nm, $c=1.360\ 4(1)$ nm, $\alpha=73.655(2)^\circ$, $\beta=69.847(1)^\circ$, $\gamma=73.026(2)^\circ$, $Z=1$, $V=1.288\ 1(2)$ nm³, $R_1=0.054\ 4$, $wR_2=0.163\ 5$. In the Co(II) complex, there are two L^{2-} moieties (which provide N_2O_2 donors), two acetate ions, two coordinated CH_3OH molecules and two non-coordinated disordered CH_3CN molecules, which result in the formation of octahedral geometries around the Co(II) atoms. And every title compound molecule links four other molecules into an infinite 2D-layer supramolecular structure via intermolecular $C-H \cdots O$ hydrogen bond interactions. CCDC: 780294.

Key words: bisoxime ligand; cobalt(II) complex; synthesis; crystal structure

Recently, a series of N,N' -bis(salicylidene)ethylenediamine (Salen) and its derivatives are regarded as the most prevalent mixed-donor ligands in the field of modern coordination chemistry because they not only exhibit diversity in structure but also have widespread application prospect in medicine^[1], catalysis^[2], analytical chemistry^[3] and magnetic properties^[4]. In addition, some of them are used as models of reaction centers of metalloenzymes^[5-6], nonlinear optical materials^[7] and present excellent catalytic activities for epoxidation,

aziridination and so on^[8-9]. Although many Salen-type complexes have been reported, the structures of Salen-type bisoxime compounds and their transition metal complexes have been rarely determined^[10-12]. In order to extend our work^[13] on structural characterization of salen-type bisoxime compounds, we reported the synthesis and structure of the title complex $[Co_3(OAc)_2(CH_3OH)_2L_2] \cdot 2CH_3CN$ ($H_2L=4,4'$ -dinitro-2,2'-[1,2-ethylenedioxybis(nitrilomethylidyne)]diphenol) in this paper.

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1 Experimental

1.1 Reagents and physical measurements

5-Nitrosalicylaldehyde from Aldrich was used without further purification. 1,2-Bis(aminooxy)ethane was synthesized according to an analogous method reported earlier^[14-16], and the other reagents and solvent were analytical grade from Tianjin Chemical Reagent Factory. Elemental analysis for Co was detected by an IRIS ER/S·WP-1 ICP atomic emission spectrometer. C, H, and N analyses were obtained using a GmbH VarioEL V3.00 automatic elemental analysis instrument. IR spectra were recorded on a VERTEX70 FTIR spectrophotometer, with samples prepared as KBr (500~4 000 cm^{-1}) or CsI (100~500 cm^{-1}) pellets. X-ray single crystal structure determination was carried out on a Bruker Smart APEX CCD diffractometer. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company, and the thermometer was uncorrected.

1.2 Synthesis

H_2L was synthesized according to the method reported earlier^[17]. Yield, 82.5%, m.p. 202~203 °C. Anal. Calcd. for $\text{C}_{16}\text{H}_{14}\text{N}_4\text{O}_8$ (%): C, 49.24; H, 3.62; N, 14.35. Found(%): C, 49.12; H, 3.59; N, 14.32.

A solution of cobalt(II) acetate tetrahydrate (2.0 mg, 0.01 mmol) in methanol (1 mL) was added dropwise to a solution of H_2L (3.0 mg, 0.01 mmol) in acetonitrile (4 mL at room temperature. The color of the mixing solution immediately turned orange-yellow and allowed to stand at room temperature for two weeks. Then the solvent partially evaporated and deep-red block-like single crystals suitable for X-ray crystallographic analysis were obtained. Anal. Calcd. for $\text{C}_{42}\text{H}_{44}\text{Co}_3\text{N}_{10}\text{O}_{22}$ (%): C, 41.43; H, 3.64; N, 11.50; Co, 14.52. Found(%): C, 41.33; H, 3.72; N, 11.52; Co, 13.55.

1.3 Crystal structure determination

The single crystal of the complex with approximate dimensions of 0.31 mm×0.17 mm×0.15 mm was placed on a Bruker Smart 1000 CCD area detector. The diffraction data were collected using a graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at 298(2) K. The LP factor and Semi-empirical absorption corrections were applied to the intensity data. The structures were solved by using the program SHELXS-97, and refined by full-matrix least-squares method on F^2 using SHELXS-97. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically. Details of the data collection and refinements of complex are given in Table 1.

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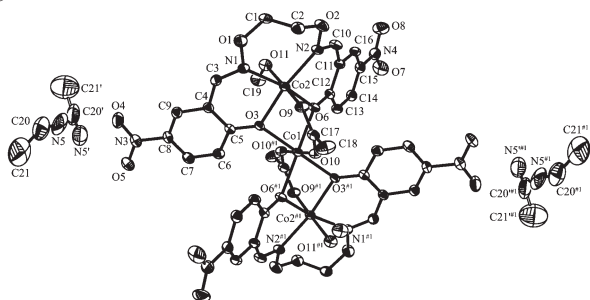
Table 1 Crystal data and structure refinement for title complex

Empirical formula	$\text{C}_{42}\text{H}_{44}\text{Co}_3\text{N}_{10}\text{O}_{22}$	$\mu(\text{Mo } K\alpha) / \text{mm}^{-1}$	1.044
Formula weight	1217.66	$F(000)$	623
Temperature / K	298(2)	Crystal size / mm	0.31×0.17×0.15
Wavelength / nm	0.071 073	θ range / (°)	1.63 to 25.02
Crystal system	Triclinic	Index ranges	$-9 \leq h \leq 11$, $-12 \leq k \leq 12$, $-16 \leq l \leq 16$
Space group	$P\bar{1}$	Reflections collected	6 710
a / nm	0.992 80(8)	Independent reflections	4 477
b / nm	1.084 4(1)	R_{int}	0.026
c / nm	1.360 4(1)	Completeness to $\theta=24.00^\circ$ / %	98.5
α / (°)	73.655(2)	Data / restraints / parameters	4 477 / 0 / 381
β / (°)	69.847(1)	GOF	1.022
γ / (°)	73.026(2)	R_1	0.054 4
Volume / nm^3	1.288 1(2)	wR_2 ($I > 2\sigma(I)$)	0.136 6
Z	1	$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}} / (\text{e} \cdot \text{nm}^{-3})$	720, -599
$D_c / (\text{Mg} \cdot \text{m}^{-3})$	1.57		

2 Results and discussion

2.1 Crystal structure

The ORTEP representation of Co(II) complex is shown in Fig.1. Selected bond lengths and angles are given in Table 2.



Symmetry code: ^{#1} $-x+1, -y+1, -z+1$; H atoms and solvent molecules are omitted for clarity

Fig.1 Crystal structures of title complex with the atom numbering with thermal ellipsoids are plotted at 30% probability level

X-ray structural study reveals that the complex crystallizes in the triclinic system, space group $P\bar{1}$. The complex consists of three Co(II) atoms, two L^{2-} units, two acetate ions, two coordinated CH_3OH molecules and two non-coordinated disordered CH_3CN molecules as expected from the analytical data. Each of the inner Co(II) atoms is hexa-coordinated. The coordination sphere of terminal Co(II) atoms (Co2) were completed by N_2O_2 (N1, N2, O3, O6) donors of L^{2-} , one oxygen atom (O9) of the acetate ion and one oxygen atom (O11) of the methanol molecule. Meanwhile, the sphere of central Co(II) atom (Co1) was completed by four l-phenolic oxygens (O3, O6, O3^{#1}, O6^{#1}) which have been deprotonated in two [CoL] chelates and two oxygen atoms (O10, O10^{#1}) of the acetate ions. Thus, that constitutes three octahedral geometries around three hexa-coordinated Co(II) atoms, respectively. And the central

Table 2 Selected bond distances (nm) and bond angles (°) for title complex

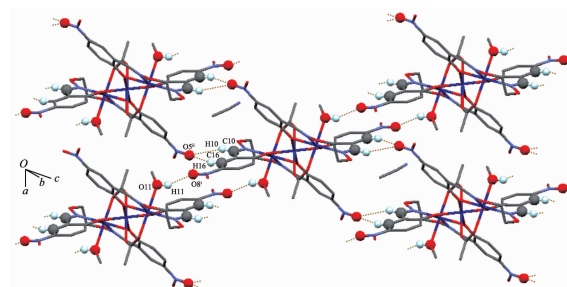
Co(1)-O(10) ^{#1}	0.204 2(4)	Co(2)-N(1)	0.212 8(4)	N(4)-O(8)	0.124 5(7)
Co(1)-O(10)	0.204 2(4)	Co(2)-O(11)	0.218 2(4)	N(4)-C(15)	0.144 7(7)
Co(1)-O(6) ^{#1}	0.212 5(3)	N(1)-C(3)	0.128 8(7)	N(5)-C(20)	0.116(3)
Co(1)-O(6)	0.212 5(3)	N(1)-O(1)	0.1425(5)	N(5')-C(20')	0.109(3)
Co(1)-O(3) ^{#1}	0.214 8(3)	N(2)-C(10)	0.128 0(7)	O(1)-C(1)	0.142 1(7)
Co(1)-O(3)	0.214 8(3)	N(2)-O(2)	0.142 5(5)	O(2)-C(2)	0.143 8(7)
Co(2)-O(6) ^{#1}	0.204 9(3)	N(3)-O(5)	0.122 5(6)	O(3)-C(5)	0.131 3(6)
Co(2)-O(9)	0.206 1(4)	N(3)-O(4)	0.122 6(6)	O(6)-C(12)	0.131 5(6)
Co(2)-O(3)	0.206 4(3)	N(3)-C(8)	0.145 3(7)	O(9)-C(17)	0.127 0(6)
Co(2)-N(2)	0.211 5(4)	N(4)-O(7)	0.122 6(7)	O(10)-C(17)	0.124 3(6)
O(10) ^{#1} -Co(1)-O(10)	180.0(2)	O(3) ^{#1} -Co(1)-O(3)	180.0(2)	N(2)-Co(2)-O(11)	87.3(2)
O(10) ^{#1} -Co(1)-O(6) ^{#1}	88.0(1)	O(6)-Co(2)-O(9)	96.2(2)	N(1)-Co(2)-O(11)	83.6(2)
O(10)-Co(1)-O(6) ^{#1}	92.0(1)	O(6)-Co(2)-O(3)	81.6(1)	O(1)-N(1)-Co(2)	128.0(3)
O(10) ^{#1} -Co(1)-O(6)	92.0(1)	O(9)-Co(2)-O(3)	89.7(2)	C(10)-N(2)-Co(2)	124.0(4)
O(10) ^{#1} -Co(1)-O(6)	88.0(1)	O(6)-Co(2)-N(2)	85.9(2)	O(2)-N(2)-Co(2)	127.3(3)
O(6)-Co(1)-O(6)	180.0(1)	O(9)-Co(2)-N(2)	93.0(2)	C(5)-O(3)-Co(2)	129.1(3)
O(10) ^{#1} -Co(1)-O(3) ^{#1}	89.1(1)	O(3)-Co(2)-N(2)	167.4(2)	C(5)-O(3)-Co(1)	133.2(3)
O(10)-Co(1)-O(3) ^{#1}	90.9(1)	O(6)-Co(2)-N(1)	165.2(2)	Co(2)-O(3)-Co(1)	95.8(1)
O(6) ^{#1} -Co(1)-O(3) ^{#1}	77.9(1)	O(9)-Co(2)-N(1)	93.2(2)	C(12)-O(6)-Co(2)	126.0(3)
O(6)-Co(1)-O(3) ^{#1}	102.1(1)	O(3)-Co(2)-N(1)	87.1(2)	C(12)-O(6)-Co(1)	133.8(3)
O(10) ^{#1} -Co(1)-O(3)	90.9(1)	N(2)-Co(2)-N(1)	105.1(2)	Co(2)-O(6)-Co(1)	97.0(1)
O(10)-Co(1)-O(3)	89.1(1)	O(6)-Co(2)-O(11)	87.1(1)	C(17)-O(9)-Co(2)	125.1(3)
O(6) ^{#1} -Co(1)-O(3)	102.1(1)	O(9)-Co(2)-O(11)	176.8(2)	C(17)-O(10)-Co(1)	133.1(4)
O(6)-Co(1)-O(3)	77.9(2)	O(3)-Co(2)-O(11)	90.8(1)	C(19)-O(11)-Co(2)	126.7(4)

Symmetry code: ^{#1} $-x+1, -y+1, -z+1$.

Co1 atom sits on a crystallographic inversion center in the crystal. Therefore, the whole Co (II) complex is rigorously centrosymmetric. In the complex, two L^{2-} units serve both as tetradentate N_2O_2 donors for the two terminal Co(II) atoms, and at the same time as bidentate moieties for the central Co(II) atom. The two acetate ions coordinated to the three Co(II) atoms via a familiar Co-O-C-O-Co coordinated mode.

The special interest of complex $[Co_3(OAc)_2(CH_3OH)_2L_2] \cdot 2CH_3CN$ is its self-assembling array linked by intermolecular hydrogen bonds (Fig.2). The hydrogen bond data are summarized in Table 3. In the crystal structure, a strong intermolecular hydrogen bond, $O11-H11 \cdots O8^{#1}$, is formed between the hydroxyl (-O11H11) of the coordinated methanol molecule and the oxygen atom (O8) of nitril group in L^{2-} unit. Simultaneously, two intermolecular hydrogen bonds, $C10-H10 \cdots O5^{#2}$ and $C16-H16 \cdots O5^{#2}$, were formed

between the oxygen atoms (O5) of nitril group in L^{2-} unit and the methylene group (-C10H10) of the oxime moiety, and the methylene (-C16H16) of the benzene ring, respectively. Thus, every title compound molecule links four other molecules into an infinite 2D-layer supramolecular structure via intermolecular hydrogen bond interactions.



Symmetry codes: $^{#1} -x, 1-y, 2-z$; $^{#2} x, y, 1+z$; H atoms are omitted for clarity

Fig.2 Part supramolecular structure containing hydrogen bonds for title complex

Table 3 Hydrogen bonding distances and bond angles for title complex

D-H \cdots A	$d(D-H)$ / nm	$d(H\cdots A)$ / nm	$d(D\cdots A)$ / nm	$\angle DHA$ / ($^\circ$)
O11-H11 \cdots O8 $^{#1}$	0.082	0.209	0.285 2(6)	155
C10-H10 \cdots O5 $^{#2}$	0.093	0.256	0.340 6(7)	152
C16-H16 \cdots O5 $^{#2}$	0.093	0.253	0.339 4(7)	155

Symmetry codes: $^{#1} -x, 1-y, 2-z$; $^{#2} x, y, 1+z$.

2.2 FTIR spectra

The FTIR spectra of H_2L and its corresponding Co(II) complex exhibit various bands in the 100~4 000 cm^{-1} region. The free ligand H_2L exhibits characteristic C=N stretching band at 1 613 cm^{-1} , while the C=N of the Co(II) complex was observed in the 1 597 cm^{-1} . The C=N stretching frequency is shifted to lower frequency by *ca.* 16 cm^{-1} upon complexation, indicating a decrease in the C=N bond order due to the coordinated bonds of the divalent cobalt atoms with the oxime nitrogen lone pair^[18]. The Ar-O stretching frequency appears as a strong band within 1 263~1 213 cm^{-1} range as reported for similar ligands^[19-20]. This band occurs at 1 236 cm^{-1} for H_2L and at 1 245 cm^{-1} for the Co(II) complex, respectively. The Ar-O stretching frequency is shifted to higher frequency, indicating that the Co-O bond was formed between the Co(II) atom and oxygen atom of phenolic group^[18,21]. In addition, a very broad

absorption band at 3 435 cm^{-1} in the Co(II) complex is assigned to -OH groups of coordinated methanol.

The far-infrared spectrum of the Co(II) complex was also obtained in the region 500~100 cm^{-1} in order to identify frequencies due to the Co-O and Co-N bonds. The IR spectrum of the Co(II) complex shows vibrational absorption frequencies at 438 and 405 cm^{-1} , which were assigned to $\nu(Co-N)$ and $\nu(Co-O)$, respectively. These assignments are consistent with the literature values^[22].

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