

不对称三芳基三氮唑的钴配合物中三氮唑-吡啶间二面角的反常变化

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摘要: 以 3-对甲氧基苯基-4-对溴苯基-5-(2-吡啶基)-1,2,4-三氮唑(L)作为配体, 合成了 1 个钴配合物 $[\text{CoL}_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$, 对其进行了红外、电喷雾质谱、热重分析和单晶结构表征, 该配合物属于单斜晶系, 空间群 $P2_1/n$, $a=0.876\ 3(5)\ \text{nm}$, $b=3.384\ 4(18)\ \text{nm}$, $c=0.920\ 3(5)\ \text{nm}$, $\beta=102.961(8)^\circ$, $V=2.660(2)\ \text{nm}^3$, $Z=2$, $R_1=0.064\ 4$ 。单晶结构表明, 钴离子处于 1 个扭曲的八面体配位环境中, 2 个水分子呈反式配位, 每个配体 L 通过三氮唑上的 1 个氮原子和吡啶氮原子参与配位。配体配位后三氮唑-吡啶间二面角反而变大。热重分析表明该配合物在 345 °C 开始发生分解。

关键词: 钴配合物; 晶体结构; 三氮唑

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Abnormal Change of Triazole-pyridyl Dihedral Angle in a Co(II) Complex with Asymmetrical Substituted Triaryltriazoles

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Abstract: A cobalt(II) complex, *trans*- $[\text{CoL}_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{C}_2\text{H}_5\text{OH}$, (L=3-(*p*-methoxyphenyl)-4-(*p*-bromophenyl)-5-(2-pyridyl)-1,2,4-triazole), was synthesized and characterized by FT-IR, ESI-MS, TGA and X-ray crystallography. The complex crystallizes in monoclinic system with space group $P2_1/n$, $a=0.876\ 3(5)\ \text{nm}$, $b=3.384\ 4(18)\ \text{nm}$, $c=0.920\ 3(5)\ \text{nm}$, $\beta=102.961(8)^\circ$, $V=2.660(2)\ \text{nm}^3$, $Z=2$ with final $R=0.064\ 4$. The cobalt atom lies in a distorted octahedral environment with two water molecules in the *trans* positions. The ligand L coordinates via one triazole nitrogen and pyridine nitrogen atom. The triazole-pyridyl dihedral angle in the complex is larger than that in the free L ligand. The TG analysis shows that the complex is stable below 345 °C. CCDC: 859546.

Key words: Co(II) complex; crystal structure; 1,2,4-triazole

0 Introduction

During the past two decades, triaryltriazoles have gained considerable attention due to their versatile coordination modes^[1] and the intriguing spin-crossover properties of their iron(II) complexes^[2-5]. Generally, in the free triaryltriazole, the three aryl rings are not coplanar with the central triazole ring. However, in the complexes of any triaryltriazole, the triazole-pyridyl

dihedral angle becomes always smaller in favor of coordination^[6-19]. Recently, we report a very unusual example that conformation change of an asymmetrical substituted triaryltriazole, 3-(*p*-methoxyphenyl)-4-(*p*-bromophenyl)-5-(2-pyridyl)-1,2,4-triazole (L), is abnormal before and after its coordination^[13], that is, the triazole-pyridyl dihedral angles in the complexes *trans*- $[\text{MnL}_2(\text{NCS})_2]$ and *trans*- $[\text{CuL}_2(\text{ClO}_4)_2]$ become larger than that in the free L ligand. As a continuation

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of our investigation on the L ligand, we present here synthesis, crystal structure, and thermal stability of *trans*-[CoL₂(H₂O)₂](ClO₄)₂·2C₂H₅OH. The abnormal change of triazole-pyridyl dihedral angle in the complex was observed again.

1 Experimental

1.1 Materials and measurements

All chemicals used were of analytical grade. Solvents were purified by conventional methods. The ligand L was prepared as reported earlier^[13]. Elemental analyses (C, H, N) were carried out with a Thermo Finnigan Flash 1112A elemental analyzer. IR spectrum was recorded on a Nicolet Avatar 380 FT-IR instrument with KBr pellets in the range of 4 000~400 cm⁻¹. Electrospray ionization mass spectrum (ESI-MS) was recorded with an LCQ ADVANTAGE MAX mass spectrometer, with MeOH on the mobile phase; the flow rate of the mobile phase was 0.2 cm³·min⁻¹. The spray voltage, the capillary voltage, and the capillary temperature were 4 kV, 40V, and 260 °C, respectively. Thermogravimetric analysis (TGA) was performed with a simultaneous NETZSCH STA 449C thermal analyzer under flowing nitrogen from 35 to 550 °C at a heating rate of 5 °C·min⁻¹.

1.2 Synthesis of *trans*-[CoL₂(H₂O)₂](ClO₄)₂·2C₂H₅OH

A solution of CoCl₂·6H₂O (0.2 mmol) in EtOH (2 mL) was added dropwise to a solution of L (0.4 mmol) in boiling anhydrous EtOH (10 mL). The mixture was

stirred for 15 min and then added a solution of NaClO₄ (0.4 mmol) in EtOH (3 mL). After refluxed 6 h, a resulting light-yellow product was filtered and washed with H₂O, and dried under vacuum to give 0.159 mmol (79.5%) of the complex. The light-yellow single crystals suitable for X-ray diffraction were obtained by evaporation from an EtOH solution. Elemental analyses calcd. for C₄₄H₄₆Br₂Cl₂CoN₈O₁₄(%): C 44.02, H 3.86, N 9.33; found(%): C 44.39, H 4.01, N 9.11. IR data (ν/cm⁻¹): 3 424 (b, w); 3 088 (w); 2 976 (w); 1 608 (m); 1 578 (w); 1 492 (m); 1 471 (s); 1 259 (s); 1 129 (s); 1 066 (m); 1 020 (m); 943 (w); 839 (m); 637 (s). ESI-MS: *m/z*=972.17; 932.25; 640.92; 524.42; 437.08.

1.3 Crystal structure determination

The well-shaped single crystals of *trans*-[CoL₂(H₂O)₂](ClO₄)₂·2C₂H₅OH were selected for X-ray diffraction study. The unit cell parameters and intensity data were collected at 296(2) K on a Bruker SMART APEX II CCD diffractometer using a graphite-monochromated Mo Kα (λ=0.071 073 nm) radiation. The structure was solved by direct methods and refined on *F*² by full-matrix least squares procedures using SHELXTL software^[20]. All non-hydrogen atoms were anisotropically refined. Atoms O2, O3, O4 and O5 of ClO₄⁻ anion were found to be highly disordered with occupancy of 0.50. All H atoms were located from a difference map and refined isotropically. Crystallographic data are summarized in Table 1.

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Table 1 Crystal data and structure refinement for the complex

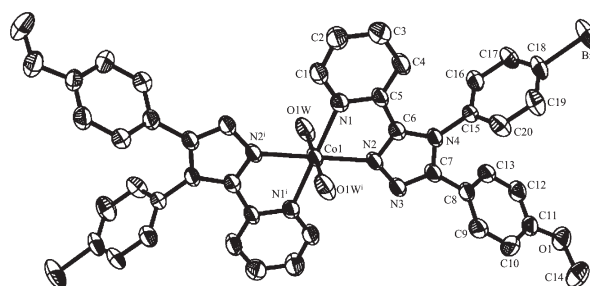
Complex	[CoL ₂ (H ₂ O) ₂](ClO ₄) ₂ ·2C ₂ H ₅ OH	<i>μ</i> / mm ⁻¹	1.993
Empirical formula	C ₄₄ H ₄₆ Br ₂ Cl ₂ CoN ₈ O ₁₄	<i>F</i> (000)	1 218
Formula weight	1 200.54	Crystal size / mm	0.20×0.12×0.10
Crystal system	Monoclinic	<i>θ</i> range / (°)	1.20~25.00
Space group	<i>P</i> 2 ₁ / <i>n</i>	Reflections collected	187 72
<i>a</i> / nm	0.876 3(5)	Independent reflections	4 689 (<i>R</i> _{int} =0.076 2)
<i>b</i> / nm	3.384 4(18)	Reflections observed (<i>I</i> >2σ(<i>I</i>))	2 245
<i>c</i> / nm	0.920 3(5)	Data / restraints / parameters	4 689 / 64 / 364
<i>β</i> / (°)	102.961(8)	Goodness-of-fit on <i>F</i> ²	0.986
<i>V</i> / nm ³	2.660(2)	<i>R</i> / <i>wR</i> (<i>I</i> >2σ(<i>I</i>))	0.064 4 / 0.164 1
<i>Z</i>	2	<i>R</i> / <i>wR</i> (all data)	0.145 7 / 0.189 7
<i>D</i> _c / (g·cm ⁻³)	1.499	Max., Min. Δρ / (e·nm ⁻³)	473, -398

2 Results and discussion

2.1 Crystal structure

A projection of the structure of *trans*-[CoL₂(H₂O)₂](ClO₄)₂·2C₂H₅OH is presented in Fig.1 together with the atomic labeling system. The complex crystallizes in the monoclinic space group *P*2₁/*n* and there is an inversion centre at the cobalt(II) atom. The crystal structure consists of a [CoL₂(H₂O)₂]²⁺ cation, two ClO₄⁻ anions, and two ethanol molecules, which is agreement with the elemental analysis result. Relevant interatomic distances and angles are given in Table 2.

The cobalt(II) atom is octahedrally coordinated by four nitrogen atoms from two L ligands in the equatorial plane and two oxygen atoms from two water molecules in the axial position. This is different from those found in the homologous Co(II) complexes, *cis*-[CoL¹₂(H₂O)₂](ClO₄)₂·2H₂O^[7] (L¹=3-(*p*-methoxyphenyl)-4-(*p*-chlorophenyl)-5-(2-pyridyl)-1, 2, 4-triazole) and *cis*-[CoL²₂(H₂O)₂](ClO₄)₂·H₂O·CH₃OH^[15] (L²=3-methyl-4-(*p*-bromophenyl)-5-(2-pyridyl)-1, 2, 4-triazole) where



Hydrogen atoms, ethanol and anions are omitted for clarity; 30% probability level for the thermal ellipsoids; Symmetry code: ⁱ 2-*x*, -*y*, 2-*z*

Fig.1 Projection of the structure of complex with the atomic labeling system

two coordinate water molecules are in a *cis* arrangement. Each L ligand coordinates to cobalt(II) atom through N atom of the pyridyl ring and one N atom of the triazole, which is similar to the coordination mode found in *cis*-[CoL¹₂(H₂O)₂](ClO₄)₂·2H₂O^[7]. The Co-O and Co-N distances are within the range observed for octahedral Co(II) complexes^[7,15,21]. However, the Co-N_{tr} bond length is 0.006 3 nm shorter than Co-

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

Co1-N1	0.214 4(5)	N2-N3	0.138 0(6)	O1-C14	0.143 4(10)
Co1-N2	0.208 1(4)	Br1-C18	0.187 3(6)		
Co1-O1W	0.205 3(5)	N4-C15	0.144 1(7)		
N1-Co1-O1W	91.2(2)	N1-Co1-O1W ⁱ	88.8(2)	N2-Co1-N2 ⁱ	180.00(11)
N2-Co1-O1W	90.4(2)	N2-Co1-O1W ⁱ	89.6(2)		
N1-Co1-N2	76.39(18)	N1-Co1-N1 ⁱ	180.00(2)		

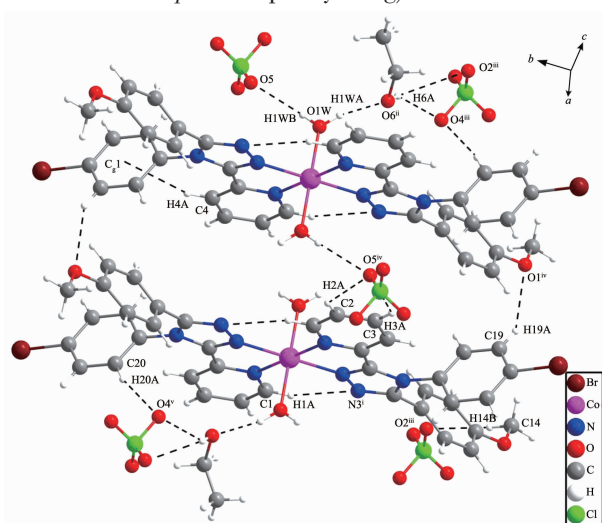
Symmetry code: ⁱ 2-*x*, -*y*, 2-*z*.

Table 3 Hydrogen bonding interactions in the complex

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠ D-H...A / (°)
O1W-H1WA...O6 ⁱⁱ	0.083(6)	0.178(5)	0.260 3(9)	167
O1W-H1WB...O5	0.084(3)	0.248(5)	0.316(2)	138
O6-H6A...O2 ⁱⁱⁱ	0.082 1(7)	0.282(4)	0.344(4)	133
O6-H6A...O4 ⁱⁱⁱ	0.082 1(7)	0.203(1)	0.268(2)	136
C1-H1A...N3 ⁱ	0.093 3(7)	0.2646(5)	0.3457(9)	146
C2-H2A...O5 ^{iv}	0.093 0(7)	0.283(2)	0.340(2)	121
C3-H3A...O5 ^{iv}	0.093 1(7)	0.266(2)	0.331(2)	127
C14-H14B...O2 ⁱⁱⁱ	0.096(1)	0.257(4)	0.353(4)	175
C19-H19A...O1 ^{iv}	0.093 1(9)	0.257 2(6)	0.320(1)	125
C20-H20A...O4 ^v	0.093 0(7)	0.266(1)	0.356(1)	165
C4-H4A...C _g 1	0.093 1(7)	0.2955	0.3798	151

Symmetry codes: ⁱ 2-*x*, -*y*, 2-*z*; ⁱⁱ 1-*x*, -*y*, 2-*z*; ⁱⁱⁱ *x*-1, *y*, *z*-1; ^{iv} 1+*x*, *y*, *z*; ^v *x*, *y*, *z*-1.

N_{py} one. The same feature has been observed in the analogous Co(II) complexes^[7,15,21]. The ligand L in the complex is non-planar. The triazole ring is oriented at dihedral angles of $4.4(2)^\circ$, $58.5(2)^\circ$ and $74.8(2)^\circ$ with respect to the pyridyl ring, the *p*-methoxyphenyl ring and *p*-bromophenyl ring, respectively. It is noticeable that on coordination, the triazole-pyridyl dihedral angle in the complex becomes larger than that observed in the free L ligand, which is very rare in the complexes of any triaryltriazole^[13]. In addition, the dihedral angles between the central 1,2,4-triazole ring and the substituted phenyl rings in the complex are smaller than those in the free L ligand^[13]. The crystal structure of the complex is further stabilized by several kinds of intermolecular and intramolecular C-H \cdots N, C-H \cdots O, O-H \cdots O hydrogen bonds and C-H \cdots C_g1 interactions (Fig.2 and Table 3, C_g1 is the centroid of the *p*-bromophenyl ring).



Symmetry codes: ⁱ 2-x, -y, 2-z; ⁱⁱ 1-x, -y, 2-z; ⁱⁱⁱ x-1, y, z-1;

^{iv} 1+x, y, z; ^v x, y, z-1

Fig.2 Hydrogen bonding interactions in the complex

2.2 Spectral characterization

In the IR spectrum of the complex, there are three bands at 1 129 (s), 943 (w) and 637 cm^{-1} (s), attributable to the IR-allowed ν mode, IR-forbidden ν mode and the non-degenerate ClO_3^- symmetrical bending frequency of the ClO_4^- anions, respectively^[15]. Broad bands around 3 424 cm^{-1} are attributed to H-O-H stretching vibrations of the water molecules. A band at 1 608 cm^{-1} (m) can be assigned to the coordinated

pyridine ring. In addition, the asymmetrical stretching frequency of Ph-Br is at 1 066 cm^{-1} (m)^[18]. These features are in agreement with the results of X-ray analysis.

The structure of *trans*-[CoL₂(H₂O)₂](ClO₄)₂·2C₂H₅OH in solution was also studied by electrospray ionization mass spectrometry (ESI-MS)^[22-23]. Fig.3 displays a positive ion ESI mass spectrum of the complex in the methanol solution. Four main peaks were observed. The peak at m/z 972.17 is [CoL₂(ClO₄)]⁺ and the base peak at m/z 932.25 is [Co(L-OCH₃+H)₂(ClO₄)]⁺ ion. The peaks at m/z 640.92 and 437.08 are assigned to [CoL₃]²⁺ and [CoL₂]²⁺ ion, respectively.

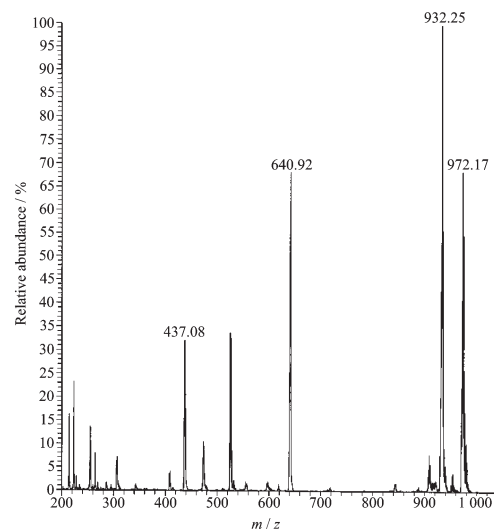


Fig.3 ESI-MS spectra of the complex

2.3 Thermal stability

TGA shows that there are two main thermal decomposition processes for the complex. The first weight loss of 10.8% in the range of 35 to 130 $^\circ\text{C}$ corresponds to removal of two ethanol molecules and two coordinated water molecules (the calculated value is 10.7%). The second abrupt weight loss is observed above 345 $^\circ\text{C}$ because of the decomposition of the ligands. The remaining weight of 6.7% after heating to 520 $^\circ\text{C}$ is due to the final residue of CoO, in agreement with the calculated value of 6.2%. The thermal decomposition feature of the complex is also in good agreement with its crystal structure.

3 Conclusions

In this paper a new cobalt(II) complex with 3-(*p*-

methoxyphenyl)-4-(*p*-bromophenyl)-5-(2-pyridyl)-1,2,4-triazole has been synthesized and characterized by elemental analyses, IR, TGA, ESI-MS spectra and X-ray crystal structure analysis. The cobalt atom is in a distorted octahedral environment and coordinated by two *trans*-oriented water molecules. Each ligand coordinates via one triazole nitrogen atom and pyridine nitrogen atom. The triazole-pyridyl dihedral angle in the complex is larger than that in the free L ligand.

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