

含有 4-对溴苯基-3,5-二(2-吡啶基)-1,2,4-三氮唑钴 配合物的合成,晶体结构和磁性

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摘要: 本文合成了一个二价钴配合物 $[\text{CoL}^5_2(\text{NCS})_2]$, (配体 L^5 =4-对溴苯基-3,5-二(2-吡啶基)-1,2,4-三氮唑)。其结构由单晶 X 衍射结构分析,红外和电喷雾离子质谱表征。该配合物晶体属于三斜晶系,空间群为 $P\bar{1}$, 钴原子和 2 个三芳基三氮唑配体的 4 个氮原子(平面)和 2 个硫氰根的氮原子(轴向)配位形成扭曲的八面体构型。磁性测定表明在 1.8~300 K 的温度范围内该配合物处于高自旋态。

关键词: 钴配合物; 晶体结构; 三氮唑; 磁性

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Synthesis, Crystal Structure and Magnetic Property of a Novel Cobalt(II) Complex with 4-(*p*-bromophenyl)-3,5-bis(2-pyridyl)-1,2,4-triazole

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Abstract: A new cobalt(II) complex, $[\text{CoL}^5_2(\text{NCS})_2]$, [L^5 =4-(*p*-bromophenyl)-3,5-bis(2-pyridyl)-1,2,4-triazole], was synthesized and its structure was determined by single crystal X-ray diffraction, FTIR and ESI-MS spectroscopy. The complex crystallizes in triclinic system with space group $P\bar{1}$. The cobalt atom is in a distorted octahedral environment with two bidentate chelating L ligands in the equatorial plane and two NCS^- ions in the axial positions. Magnetic measurements show that the complex is in a high-spin state in the 1.8~300 K range. CCDC: 668715.

Key words: cobalt(II) complex; crystal structure; triazole; magnetic property

Substituted 1,2,4-triazole is a very useful ligand in coordination chemistry^[1]. This is mainly because of the fact that the 1,2,4-triazole systems can act as bridging ligands between transition metal ions thus promising rich and versatile coordination modes. More interestingly, some iron (II) complexes with the substituted 1,2,4-triazoles have spin-crossover properties which can be used as molecular electronics^[2], memory

devices^[3], information storage^[4] and switching materials^[5]. However, compared with alkyl-substituted 1,2,4-triazole, complexes containing triaryltriazole ligand have been rarely studied up to now^[6]. Recently, some new triaryltriazole compounds^[7-14] (Scheme 1) and their complexes^[15-22] have been prepared by us and the other workers. However, coordination compounds with 4-(*p*-bromophenyl)-3,5-bis(2-pyridyl)-1,2,4-triazole (L^5)^[8]

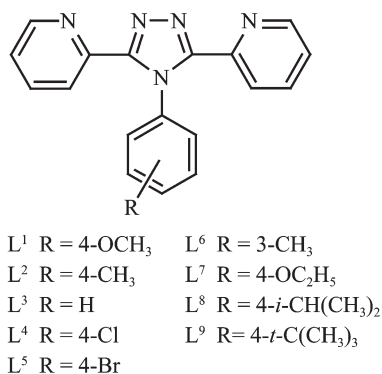
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which was synthesized in 1998 have not been observed so far. This paper deals with the first complex with the ligand L^5 . We report here the synthesis, crystal structure and magnetic property of a new cobalt (II) complex with the ligand L^5 : $[\text{Co}L^5_2(\text{NCS})_2]$.



Scheme 1

1 Experimental

1.1 Materials and measurements

All chemicals used were of analytical grade. Solvents were purified by conventional methods. The ligand (L^5) was prepared as reported earlier^[8]. Elemental analyses were performed with a Perkin-Elmer 240 instrument. FTIR spectrum was recorded on a Vector 22 Brüker spectrometer with KBr pellets in the 4 000~400 cm⁻¹ region. Electrospray ionization mass spectrum (ESI-MS) was recorded with an Agilent 1100 LC/MSD SL spectrometer, with MeOH on the mobile phase; the flow rate of the mobile phase was 0.2 cm³·min⁻¹. The capillary voltage and temperature was 2 500 V and 325 °C, respectively. The flow of nebulizer gas and dry gas is 12 and 8 cm³·min⁻¹, respectively. Variable temperature magnetic susceptibilities of crystalline of the complex were measured on a Quantum Design MPMS SQUID-XL7 magnetometer in the temperature range of 1.8~300 K. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

1.2 Synthesis of $[\text{Co}L^5_2(\text{NCS})_2]$

To a solution of KSCN (0.4 mmol) in anhydrous MeOH (3 mL) was added a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.2

mmol) in MeOH (2 mL). The mixture was stirred for 15 min and filtered. The KCl precipitate was washed with 2 mL of anhydrous MeOH. The methanolic fractions containing $\text{Co}(\text{SCN})_2$ were collected, and then was added dropwise to a solution of the L^5 (0.4 mmol) in MeOH (5 mL). A light-yellow microcrystalline product, which formed immediately, was filtered and washed with H₂O, and dried under vacuum to give 0.132 g (71%) of the complex. The light-yellow single crystals suitable for X-ray diffraction were obtained by evaporation from an acetonitrile solution. Elemental analyses [Found(%): C 49.12, H 2.82, N 18.31. $\text{C}_{38}\text{H}_{24}\text{Br}_2\text{CoN}_{12}\text{S}_2$ calcd. (%): C 48.99, H 2.60, N 18.05]. IR (cm⁻¹): $\nu(\text{CN})$ 2 071.8vs; ν (py ring) 1 601s, 1 585m, 1 571w; δ (ph ring) 832.1m, 794.2s; ν (Ar-Br) 1 068m. ESI-MS: m/z 873.1, 597.1, 514.0, 407.6, 380.2.

1.3 Crystal structure determination

A light-yellow plate crystal of the complex was selected for lattice parameter determination and collection of intensity data at 293 K on a FR590 CAD4 four-circle diffractometer with monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\,073$ nm) using a $\theta\sim 2\theta$ scan mode. The data was corrected for Lorentz and polarization effects after data reduction. An empirical absorption correction based on ψ scans was applied. The structure was solved by the direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL version 6.10^[23]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms for C-H were placed in calculated positions (C-H, 0.096 nm) and assigned fixed isotropic thermal parameters at 1.2 times of the equivalent isotropic U of the C atoms to which they are attached. The contribution of these hydrogen atoms was included in the structure factor calculations. All computations were carried out using the SHELXTL program package. Analytical anomalous dispersion corrections were incorporated. Crystallographic data for the complex are summarized in Table 1.

CCDC: 668715.

Table 1 Crystallographic data for the complex

Empirical formula	$\text{C}_{38}\text{H}_{24}\text{Br}_2\text{CoN}_{12}\text{S}_2$	Z	1
Formula weight	931.56	$D_c / (\text{Mg} \cdot \text{m}^{-3})$	1.65

Continued Table 1

Temperature / K	293(2)	$F(000)$	465
Crystal size / mm	0.20 × 0.15 × 0.10	Absorption coefficient / mm ⁻¹	2.747
Crystal color, shape	Light-yellow, plate	θ range / (°)	1.54~25.00
Crystal system	Triclinic	Index range (h, k, l)	(-9/9, -10/10, 0/15)
Space group	$P\bar{1}$	Reflections collected	3 175
a / nm	0.821 65(8)	Independent reflections	3 175
b / nm	0.867 37(10)	Data / restraints / parameters	3 175 / 139 / 214
c / nm	1.332 35(15)	Goodness-of-fit on F^2	0.943
α / (°)	95.20(3)	Final R, wR indices [$I > 2\sigma(I)$]	0.0774, 0.1498
β / (°)	92.23(3)	R, wR indices (all data)	0.177 5, 0.189 7
γ / (°)	96.80(3)	Largest diff. peak and hole / (e ⁻ ·nm ⁻³)	532 and -631
V / nm ³	0.937 79(18)		

2 Results and discussion

2.1 Synthesis

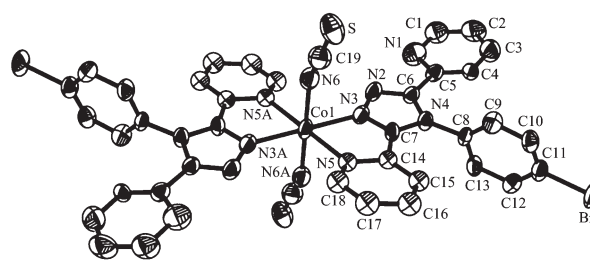
The triaryltriazole ligand L^5 reacts with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and KSCN in molar ratio 2:1:2 to form a neutral mononuclear hexacoordinate complex of formula $[\text{Co}L^5_2(\text{NCS})_2]$, which is stable in air. Yield for the complex is 71%. The elemental analysis was satisfactory and indicates that the complex contains one cobalt atom, two L^5 ligands, two thiocyanate groups.

2.2 Crystal structure

Fig.1 presents an OPTeP^[24] plot of the complex with its atom numbering scheme. The complex crystallizes in the triclinic space group $P\bar{1}$ and there is an inversion center at the cobalt(II) atom. The crystal structure consists of $[\text{Co}L^5_2(\text{NCS})_2]$, which is consistent with the elemental analysis result. Relevant interatomic distances and angles are given in Table 2.

The cobalt atom is surrounded by four nitrogen atom from two L^5 ligands in the equatorial plane and two nitrogen atoms from two NCS^- ions in the axial positions

to form a distorted octahedral geometry. The NCS^- group is almost linear [$\text{N}(6)\text{-C}(19)\text{-S}$ 178.0(11)°], and the Co-N-C(S) linkage is bent [$\text{Co-N}(6)\text{-C}(19)$ 158.7(9)°], the angle is larger than those found in some analogous *trans*- NCS^- metal(II) complexes, for example, 148.3(3)° for $[\text{Fe}L^2_2(\text{NCS})_2]$ ^[5], 147.8(3)° for $[\text{Mn}L^2_2(\text{NCS})_2]$ ^[15], but smaller than that [172.4(4)°] observed in a *trans*- $[\text{Co}L^2_2(\text{NCS})_2] \cdot 2\text{CH}_2\text{Cl}_2$ complex^[16], [$L^2=4\text{-(}p\text{-methylphenyl)-3,5-bis(2-pyridyl)-1,2,4-triazole}$]. It is worthwhile to note that Co-N(CS) bond length [0.210 1(9) nm] is equal to Co-N(trz) distance [0.210 1(8) nm]. This result is different



Symmetry code: A: $-x, 2-y, -z$

Fig.1 Structure of $[\text{Co}L^5_2(\text{NCS})_2]$, H atoms are omitted for clarity

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

Co(1)-N(6)	0.210 1(9)	N(3)-C(7)	0.130 9(10)	N(6)-C(19)	0.118 5(12)
Co(1)-N(3)	0.210 1(8)	N(5)-C(14)	0.137 5(11)	C(19)-S	0.156 7(13)
Co(1)-N(5)	0.215 8(7)	N(5)-C(18)	0.132 2(12)		
N(3)-N(2)	0.137 0(10)	N(4)-C(8)	0.143 8(10)		
Co(1)-N(6)-C(19)	158.7(9)	N(5)-Co(1)-N(3)	76.6(3)	N(3)-Co(1)-N(3A)	180.000(1)
N(6)-Co(1)-N(6A)	180.0(4)	N(5)-Co(1)-N(5A)	180.000(1)	N(6)-C(19)-S	178.0(11)
N(6)-Co(1)-N(5)	87.8(3)	N(6)-Co(1)-N(3)	90.0(3)		

Symmetry codes: A: $-x, 2-y, -z$.

from those found in two homologous cobalt(II) complexes, *trans*-[CoL₂(NCS)₂]^[21] [L¹=4-(*p*-methoxyphenyl)-3,5-bis(2-pyridyl)-1,2,4-triazole] and *trans*-[CoL₂(NCS)₂], where the Co-N(CS) bond distance is shorter than the Co-N(trz) one. In addition, the Co-N(CS) bond distance is also shorter than Co-N(py) one, which is similar to the features in complexes [CoL₂(NCS)₂] and [CoL₂(NCS)₂]. The coordination mode of the ligand (L⁵) is the same as those of the triaryltriazoles found in complexes [CoL₂(NCS)₂] and [CoL₂(NCS)₂]. The pyridyl ring where nitrogen atom is involved in coordination makes an angle of 9.4(8)° with respect to the triazole ring, whereas the non-coordinating pyridyl ring makes an angle of 13.5(8)° with respect to the triazole ring. The similar features are 14.6(4)°, 45.0(4)° and 11.7(2)°, 40.7(1)° found in the complexes [CoL₂(NCS)₂] and [CoL₂(NCS)₂], respectively.

2.3 Spectral characterization

2.3.1 FTIR spectra

The IR spectrum of [CoL₂(NCS)₂] is similar to those observed for the related complexes [CoL₂(NCS)₂]·2CH₂Cl₂^[16] and [MnL₂(NCS)₂]^[15]. A very strong band at 2 071.8 cm⁻¹ is assigned to C≡N stretching vibrations

of two *trans*-oriented thiocyanate groups. A band at 1 601 cm⁻¹ (s) and two bands at 1 585(m) and 1 571 cm⁻¹ (w) can be assigned to one coordinated and one uncoordinated pyridine ring, respectively. This means that in this complex, the ligand L⁵ use one pyridine nitrogen and one triazole nitrogen for chelate binding. In addition, the diagnostic symmetrical stretching frequency of Ar-Br is at 1 068 cm⁻¹ (m). The C-H out of plane absorption of the *para*-substituted phenyl is located around 832.1(m) and 794.2 cm⁻¹ (s). The triazole out-of-plane ring absorption is observed at 637.3 cm⁻¹ (m).

2.3.2 ESI-MS spectrum

The structure of [CoL₂(NCS)₂] in solution was also studied by electrospray ionization mass spectrometry (ESI-MS)^[25-27]. Fig.2 displays a positive ion ESI mass spectrum of the complex in the methanol solution. The base peak at *m/z* 873.1 is [CoL₂(NCS)]⁺ ion and the peak at *m/z* 597.1 is [CoL₃]⁺. The peak at *m/z* 514.0 is assigned to [CoL⁵(NCS)(H₂O)]⁺, which indicates that [CoL⁵(NCS)]⁺ structure unit combine with a H₂O molecule. The peaks at *m/z* 407.6 and 380.2 are [CoL₂]⁺ and (L⁵+2)⁺, respectively.

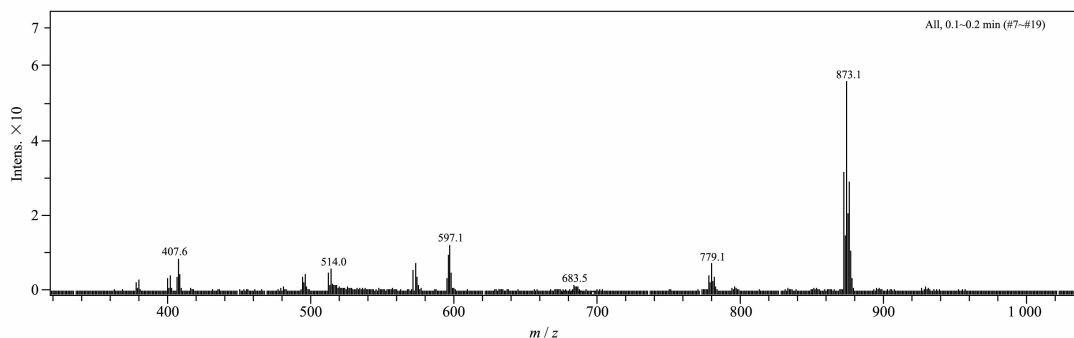


Fig.2 Positive ion ESI mass spectrum of the complex in methanol solution

2.4 Magnetic property

The temperature dependence of the molar magnetic susceptibility of [CoL₂(NCS)₂] is depicted in Fig.3 in the form of χ_m and χ_m^{-1} vs *T*. The result reveals that the complex is paramagnetic at 1.8~300 K range, which indicates that the cubic crystal-field splitting ($\Delta=10 Dq$) is lower than the electron pairing energy (*P*). For the high-spin complex a magnetic moment of 4.96 B.M./Co²⁺ is observed, as expected for an ion with ⁴T₁ ground term. The μ_{eff} value is in the normal

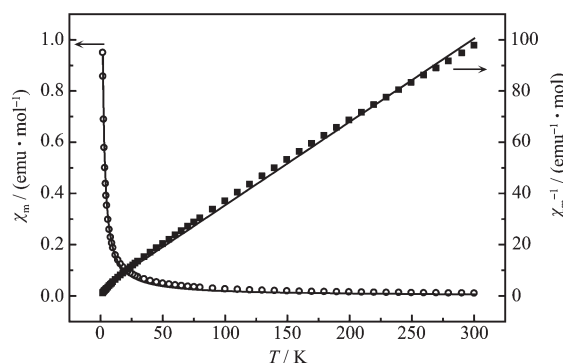


Fig.3 χ_m (○) and χ_m^{-1} (■) vs *T* plot for [CoL₂(NCS)₂]

range observed for a high-spin cobalt(II) complex ($\mu_{\text{eff}}=4.3 \sim 5.2$ B.M.) of O_h symmetry. According to the Curie-Weiss law, $\chi_m=C/(T-\theta)$, the data are in a good linear relationship between χ_m^{-1} vs T . The complex is antiferromagnetic with $C=3.07$ (2) and $\theta=-8.7$ (9) K. Current works seeks to investigate further the coordination of the ligand L^5 to other transition metal ions, especially to iron(II) ion, in order to find new spin-crossover complexes.

3 Conclusions

In this paper a new cobalt(II) complex with triaryltriazole ligand has been synthesized and characterized by elemental analyses, IR, ESI-MS spectra and X-ray diffraction crystal structure analysis. The cobalt atom is in a distorted octahedral environment and is coordinated by two *trans*-oriented thiocyanate anions. Each triaryltriazole entity coordinates via one triazole nitrogen atom and one pyridine nitrogen atom. Magnetic measurements show that the complex is high-spin species in the 1.8~300 K range.

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