

新的含有 4-对甲基苯基-3,5-二(2-吡啶基)-1,2,4-三氮唑钴配合物的合成和晶体结构

朱敦如^{*,1} 王作祥² 宋 军¹ 李一志³ 兰大艳²

(¹ 南京工业大学化学系, 南京 210009)

(² 东南大学化学化工系, 南京 210096)

(³ 南京大学配位化学国家重点实验室, 配位化学研究所, 南京 210093)

关键词: 钴配合物; 晶体结构; 三氮唑

中图分类号: O614.81²

文献标识码: A

文章编号: 1001-4861(2005)01-0128-05

Synthesis and Crystal Structure of a New Cobalt(II) Complex with 4-(*p*-methylphenyl)-3,5-bis(pyridin-2-yl)-1,2,4-triazole

ZHU Dun-Ru^{*,1} WANG Zuo-Xiang² SONG Jun¹ LI Yi-Zhi³ LAN Da-Yan²

(¹Department of Chemistry, Nanjing University of Technology, Nanjing 210009)

(²Department of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096)

(³Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093)

Abstract: A new cobalt(II) complex, $[\text{CoL}_2(\text{NCS})_2] \cdot 2\text{CH}_2\text{Cl}_2$, $[\text{L}=4\text{-(}p\text{-methylphenyl)-3,5-bis(pyridin-2-yl)-1,2,4-triazole}]$, was synthesized and its crystal structure was determined by X-ray analysis. The complex crystallizes in monoclinic system with space group $P2_1/c$, $a=0.867\ 40(17)$, $b=1.453\ 9(3)$, $c=1.781\ 9(4)$ nm, $\beta=91.18(3)^\circ$, $V=2.246\ 7(8)$ nm³ and $Z=2$. 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. CCDC: 251658.

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

0 Introduction

The coordination chemistry of substituted 1,2,4-triazoles has received considerable attention in latest decade due to the fact that some of their complexes have spin-crossover properties which can be used as molecular-based memory devices, displays and switching materials^[1~10]. Complexes with triaryltriazole ligands, however, are largely unexplored in comparison with those with the substituted 1,2,4-triazoles up to now^[11]. Recently we have prepared some new triaryl-

triazole compounds^[12~15], which can act as doubly-bidentate chelating ligands because of their structural similarity to 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (ABPT)^[16]. It is to be anticipated that the triaryl-triazoles resulting from replacement of 4-amino group of the ligand (ABPT) by a *p*-substituted aryl group would introduce a variable structural chemistry into their complexes. Recently we have reported the syntheses, crystal structures and properties of new iron(II), cobalt(II), nickel(II) and manganese(II) complexes with

收稿日期: 2004-07-12。收修改稿日期: 2004-11-04。

南京工业大学科研启动基金资助项目(No.51301031)。

*通讯联系人。E-mail: zhudr@njut.edu.cn

第一作者: 朱敦如, 男, 41 岁, 博士, 教授; 研究方向: 分子材料和配位化学。

the ligand L^[17-19]. As a continuation of our investigation of this ligand, here we present the synthesis, crystal structure of a new cobalt(II) complex with ligand L: $[\text{CoL}_2(\text{NCS})_2] \cdot 2\text{CH}_2\text{Cl}_2$.

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^[18]. Elemental analyses were performed with a Perkin-Elmer 240 instrument. IR spectrum was recorded on a Nicolet 170SX FTIR instrument (KBr discs) in the 4 000~400 cm^{-1} region. Electrospray ionization mass spectrum (ESI-MS) was recorded with a Finnigan mat APISSQ 710 mass spectrometer, with MeOH on the mobile phase; the flow rate of the mobile phase was 0.2 $\text{cm}^3 \text{min}^{-1}$. The spray voltage was 4.55 kV and the capillary voltage was 28.76 V. The capillary temperature was 200 $^\circ\text{C}$.

1.2 Synthesis of $[\text{CoL}_2(\text{NCS})_2] \cdot 2\text{CH}_2\text{Cl}_2$

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 (0.4 mmol) in MeOH (5 mL). A light-yellow microcrystalline product, which formed immediately, was filtered and washed with H_2O , and dried under vacuum to give 0.15 g (94%) of the complex. The orange single crystals suitable for X-ray diffraction were obtained by using *n*-hexane diffusion into dichloromethane solution. (Found(%): C, 52.14; H, 3.77; N, 16.98. $\text{C}_{42}\text{H}_{34}\text{Cl}_4\text{CoN}_{12}\text{S}_2$ calcd.: C, 51.91; H, 3.53; N, 17.30). IR (cm^{-1}): $\nu(\text{CH}_3)$ 2 914.5w; $\nu(\text{CN})$ 2 075.1vs; $\nu(\text{py ring})$ 1 600s, 1 585m, 1 571.6w; $\delta(\text{ph ring})$ 826.6s, 795.3s. ESI-MS: m/z 743.1, 499.2, 461.8, 431, 358.1, 342.8, 314.3.

1.3 Crystal structure determination

The orange block crystals 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 monochromated Mo $K\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$) using a $\theta\sim 2\theta$ scan mode.

The data was corrected for Lorenz and polarization effects during 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 5.10^[20]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms for C-H and O-H were placed in calculated positions (C-H, 0.096 nm) and located from different map, respectively, assigned fixed isotropic thermal parameters at 1.2 times for CH and 1.5 times for CH_3 and H_2O the equivalent isotropic U of the atoms to which they are attached, and allowed to ride on their respective parent atoms except O atoms. The contribution of these hydrogen atoms was included in the structure factor calculations. All computations were carried out on a PC-586 computer using the SHELXTL-PC program package. Analytical anomalous dispersion corrections were incorporated. Crystallographic data for the complex are summarized in Table 1.

Table 1 Crystallographic data for the complex

Empirical formula	$\text{C}_{42}\text{H}_{34}\text{Cl}_4\text{CoN}_{12}\text{S}_2$
Formula weight	971.66
Temperature / K	293(2)
Crystal size / mm	$0.32 \times 0.20 \times 0.12$
Crystal color, shape	Orange, block
Crystal system	Monoclinic
Space group	$P2_1/c$
a / nm	0.867 40(17)
b / nm	1.453 9(3)
c / nm	1.781 9(4)
β / $^\circ$	91.18(3)
V / nm^3	2.246 7(8)
Z	2
D_c / ($\text{Mg} \cdot \text{m}^{-3}$)	1.436
$F(000)$	994
Absorption coefficient / mm^{-1}	0.759
θ range / $^\circ$	1.81~25
Index range (h, k, l)	(-10/10, 0/17, 0/21)
Reflections collected	3 958
Independent reflections	3 957 [$R(\text{int})=0.043$ 1]
Data/restraints/parameters	3 957/0/277
Goodness-of-fit on F^2	1.042
final R , wR indices [$I > 2\sigma(I)$]	0.061 6, 0.144 7
R , wR indices (all data)	0.084 1, 0.149 6
Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	834 and -497

CCDC: 251658.

2 Results and discussion

2.1 Synthesis

The triaryltriazole ligand **L** reacts with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and KSCN in molar ratio 2:1:2 to form a neutral monomeric hexacoordinate complex of formula $[\text{CoL}_2(\text{NCS})_2] \cdot 2\text{CH}_2\text{Cl}_2$, which is stable in air. Yield for the complex is 94%. The elemental analysis was satisfactory and indicates that the complex contains one cobalt atom, two **L** ligands, two thiocyanate groups and two dichloromethane solvents. The ligand **L** does not seem to have any binucleating tendency towards cobalt.

2.2 Crystal structure

Fig.1 presents an ORTEP^[21] plot of the complex with its atom numbering scheme. The complex crystallizes in the monoclinic space group $P2_1/c$ and there is an inversion center at the cobalt(II) atom. The crystal structure consists of $[\text{CoL}_2(\text{NCS})_2] \cdot 2\text{CH}_2\text{Cl}_2$, which is consistent with the elemental analysis result. Relevant interatomic distances and angles are given in Table 2.

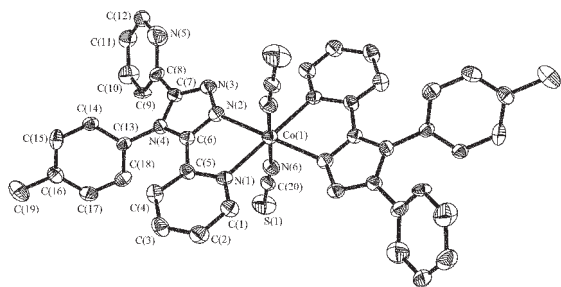


Fig.1 ORTEP diagram and atomic labelling system of $[\text{CoL}_2(\text{NCS})_2] \cdot 2\text{CH}_2\text{Cl}_2$

H atoms and the solvents are omitted for clarity.

The cobalt atom is surrounded by four nitrogen atoms from two **L** 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^- groups are almost linear $[\text{N}(6)-\text{C}(20)-\text{S}(1) 178.4(4)^\circ]$, and the $\text{Co}-\text{N}-\text{C}(\text{S})$ linkages are a few bent $[\text{Co}(1)-\text{N}(6)-\text{C}(20) 172.4(4)^\circ]$, which deviates even fewer from 180° than in other analogous *trans*- NCS^- metal(II) complexes, for example, $148.3(3)^\circ$ for $[\text{FeL}_2(\text{NCS})_2]$ ^[17] and $147.8(3)^\circ$ for $[\text{MnL}_2(\text{NCS})_2]$ ^[19]. $\text{Co}-\text{N}(\text{CS})$ bond lengths $[0.207 1(4) \text{ nm}]$ are shorter than $\text{Co}-\text{N}(\text{L})$ and those $[0.215 6(5) \text{ nm}]$ and $[0.209 4(4) \text{ nm}]$ observed in a related manganese(II) complex with 4-(*p*-methoxyph-

Table 2 Selected bond distances (nm) and angles ($^\circ$) for complex

$\text{Co}(1)-\text{N}(1)$	0.218 0(4)
$\text{Co}(1)-\text{N}(2)$	0.213 2(3)
$\text{Co}(1)-\text{N}(6)$	0.207 1(4)
$\text{N}(1)-\text{C}(5)$	0.134 8(5)
$\text{N}(1)-\text{C}(1)$	0.131 0(5)
$\text{N}(2)-\text{C}(6)$	0.133 2(5)
$\text{N}(2)-\text{N}(3)$	0.137 3(5)
$\text{N}(4)-\text{C}(13)$	0.145 2(5)
$\text{N}(6)-\text{C}(20)$	0.114 5(5)
$\text{S}(1)-\text{C}(20)$	0.162 0(4)
$\text{Co}(1)-\text{N}(6)-\text{C}(20)$	172.4(4)
$\text{N}(6)-\text{Co}(1)-\text{N}(6)^a$	180.0(2)
$\text{N}(6)-\text{Co}(1)-\text{N}(1)$	90.8(1)
$\text{N}(2)-\text{Co}(1)-\text{N}(1)$	75.6(1)
$\text{N}(1)-\text{Co}(1)-\text{N}(1)^a$	180.0
$\text{N}(6)-\text{Co}(1)-\text{N}(2)$	94.0(1)
$\text{N}(2)-\text{Co}(1)-\text{N}(2)^a$	180.0
$\text{N}(6)-\text{C}(20)-\text{S}(1)$	178.4(4)

Symmetry code: $a -x, -y, -z$.

enyl)-3,5-bis(pyridin-2-yl)-1,2,4-triazole (**L**^{*}), $[\text{MnL}^*(\text{H}_2\text{O})_2(\text{NCS})_2]$ where the two NCS^- anions are *cis*-oriented^[22]. The coordination mode of the ligand (**L**) is the same as those found in the related spin-crossover iron(II) complex $[\text{FeL}_2(\text{NCS})_2]$ ^[17] and the high-spin manganese(II) complex $[\text{MnL}_2(\text{NCS})_2]$ ^[19]. However, in present complex $[\text{CoL}_2(\text{NCS})_2] \cdot 2\text{CH}_2\text{Cl}_2$ the $\text{Co}-\text{N}$ bond to the triazole nitrogen is 0.005 nm shorter than that to the pyridyl nitrogen. The pyridyl ring where nitrogen atom is involved in coordination makes an angle of $14.6(4)^\circ$ with respect to the triazole ring, whereas the non-coordinating pyridyl ring makes an angle of $45.0(4)^\circ$ with respect to the triazole plane. The similar features are 0.002 nm, $11.6(3)^\circ$ and $14.8(3)^\circ$ found in the complex $[\text{FeL}_2(\text{NCS})_2]$, respectively.

2.3 Spectral characterization

2.3.1 FTIR spectra

The IR spectrum of $[\text{CoL}_2(\text{NCS})_2] \cdot 2\text{CH}_2\text{Cl}_2$ is similar to those observed for the related complexes $[\text{FeL}_2(\text{NCS})_2]$ ^[17] and $[\text{MnL}_2(\text{NCS})_2]$ ^[19]. A very strong band at 2075.1 cm^{-1} is assigned to $\text{C} \equiv \text{N}$ stretching vibrations of two *trans*-oriented thiocyanate groups. A band at 1600 cm^{-1} (s) and two bands at $1585(\text{m})$ and 1571.6 cm^{-1} (w) can be assigned to one coordinated and one

uncoordinated pyridine ring, respectively. The C-H out of plane absorption of the para-substituted phenyl is located around 826.6 (s) and 795.3 cm^{-1} (s). The triazole out-of-plane ring absorption is observed at about 641.5 cm^{-1} (m).

2.3.2 ESI-MS spectrum

The structure of $[\text{CoL}_2(\text{NCS})_2] \cdot 2\text{CH}_2\text{Cl}_2$ in solution was also studied by electrospray ionization mass spectrometry (ESI-MS)^[23-25]. Fig.2 displays a positive ion ESI mass spectrum of the complex in the methanol solution. The peak at m/z 743.1 is $[\text{CoL}_2(\text{NCS})]^+$ ion and base peak at m/z 499.2 is $[\text{CoL}_3]^+$. The peaks at m/z 461.8 and 358.1 are assigned to $[\text{CoL}(\text{NCS})(\text{CH}_3\text{OH})]^+$ and $[\text{CoL}_2(\text{CH}_3\text{OH})]^+$, respectively, which indicate that $[\text{CoL}(\text{NCS})]$ and $[\text{CoL}_2]$ structure units both combine with a solvent molecule. The peaks at m/z 431.0 and 342.8 are $[\text{CoL}(\text{NCS})]^+$ and $[\text{CoL}_2]^+$, respectively. Finally, the peak at m/z 314.3 is $(\text{L} + 1)^+$.

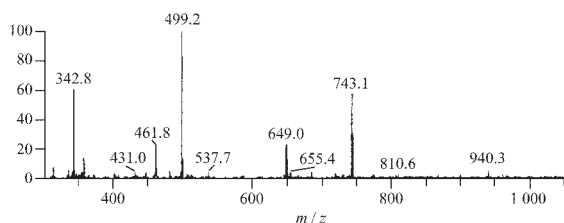


Fig.2 Positive ion ESI mass spectrum of the complex in methanol solution

2.4 Magnetic property

The temperature variation of the magnetic susceptibility in the form of χ_m and χ_m^{-1} versus T is shown in Fig.3 for $[\text{CoL}_2(\text{NCS})_2] \cdot 2\text{CH}_2\text{Cl}_2$. The result suggests that the complex is paramagnetic at 75~300 K range, which indicates that the cubic crystal-field splitting ($\Delta=10 \text{ Dq}$) is lower than the electron pairing energy (P). For the high-spin complex a magnetic moment of 4.17 B.M./ Co^{2+} is observed, as expected for an ion with 4T_1 ground term. The μ_{eff} value is in the normal range observed for a high-spin cobalt(II) complex ($\mu_{\text{eff}}=4.3 \sim 5.2 \text{ B.M.}$) 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} versus T . The complex is antiferromagnetic with $C=2.19(1)$ and $\theta=-3.3(8) \text{ K}$. Although the coordination environment of the complex is almost similar to those found in the spin-crossover complex $[\text{FeL}_2(\text{NCS})_2]$ ^[17], $[\text{CoL}_2(\text{NCS})_2] \cdot 2\text{CH}_2\text{Cl}_2$ does not show any spin-crossover phenomenon. Therefore

spin-crossover effect is very sensitive to variation of local environment.

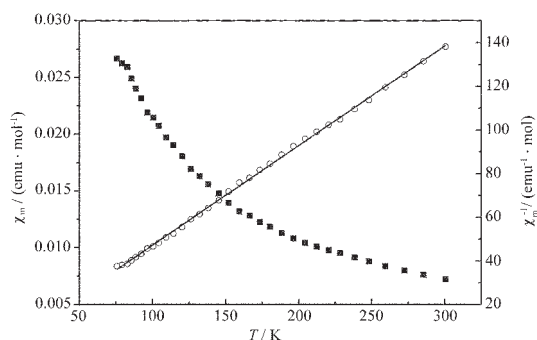


Fig.3 χ_m (■) and χ_m^{-1} (○) versus T plot for $[\text{CoL}_2(\text{NCS})_2] \cdot 2\text{CH}_2\text{Cl}_2$

3 Conclusion

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 crystallography. The cobalt atom is in a distorted octahedral environment. Two *trans*-oriented thiocyanate anions coordinate to the cobalt atom. 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 75~300 K range.

References:

- [1] Moliner N, Muñoz M C, van Koningsbruggen P J, et al. *Inorg. Chim. Acta*, **1998**,**274**:1~6
- [2] Moliner N, Muñoz M C, Létard S., et al. *Inorg. Chim. Acta*, **1999**,**291**:279~288
- [3] Moliner N, Gaspar A B, Muñoz M C, et al. *Inorg. Chem.*, **2001**,**40**:3986~3991
- [4] Vos G, Haasnoot J G, Verschoor G C, et al. *Inorg. Chim. Acta*, **1985**,**105**:31~39
- [5] Garcia Y, van Koningsbruggen P J, Bravic G, et al. *Inorg. Chem.*, **1997**,**36**:6357~6365
- [6] Rietmeijer F J, van Albada G A, de Graaff R A G, et al. *Inorg. Chem.*, **1985**,**24**:3597~3601
- [7] van Koningsbruggen P J, van Hal J W, de Graaff R A G, et al. *J. Chem. Soc., Dalton Trans.*, **1993**:2163~2167
- [8] Vos G, le Fèvre R A, de Graaff R A G, et al. *J. Am. Chem. Soc.*, **1983**,**105**:1682~1683
- [9] van Albada G A, de Graaff R A G, Haasnoot J G, et al. *Inorg. Chem.*, **1984**,**23**:1404~1408
- [10] Groeneveld L R, Vos G, Verschoor G C, et al. *Chem. Commun.*,

- 1982**:620~621
- [11]Klingele M H, Brooker S. *Coord. Chem. Rev.*, **2003**,**241**:119~132
- [12]Wang Z X, Bai Z P, Yang J X, et al. *Acta Crystallogr.*, **1998**, **C54**:438~439
- [13]Chen W, Wang Z X, Jian F F, et al. *Acta Crystallogr.*, **1998**, **C54**:851~852
- [14]Fun H K, Chinnakali K, Shao S C, et al. *Acta Crystallogr.*, **1999**,**C55**:770~772
- [15]ZHU Dun-Ru(朱敦如). *Thesis for the Doctorate of Nanjing University*(南京大学博士论文). **2000**.
- [16]Keij F S, de Graaff R A G, Haasnoot J G, et al. *J. Chem. Soc., Dalton Trans.*, **1984**:2093~2097
- [17]Zhu D, Xu Y, Yu Z, et al. *Chem. Mater.*, **2002**,**14**:838~843
- [18]Zhu D R, Song Y, Xu Y, et al. *Polyhedron*, **2000**,**19**:2019~2025
- [19]ZHU Dun-Ru(朱敦如), WANG Tian-Wei(王天维), ZHONG Sheng-Lai(仲盛来), et al. *Wuji Huaxue Xuebao*(*Chin. J. Inorg. Chem.*), **2004**,**20**:508~512
- [20]Sheldrick G M. *SHELXTL, Structure Determination Software Programs*. Version 5.10. Bruker Analytical X-ray Systems Inc., Wisconsin, USA, **1997**.
- [21]Johnson C K. *ORTEPII, Report ORNL-5138*, Oak Ridge National Laboratory, Tennessee, **1976**.
- [22]Zhu D, Xu Y, Mei Y, et al. *J. Mol. Struct.*, **2001**,**559**:119~125
- [23]Xu L, Chen X T, Xu Y, et al. *J. Mol. Struct.*, **2001**,**559**:361~368
- [24]Wilson S R, Yasmin A, Wu Y. *J. Org. Chem.*, **1992**,**57**:6941~6945
- [25]Arakawa R, Matsuo T, Ito H, et al. *Org. Mass Spectrom.*, **1994**,**29**:289~294