第 35 卷第 5 期
2019 年 5 月

无 机 化 学 学 报
CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol.35 No.5
910-914

五配位单核钴配合物的单晶结构和磁性能

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摘要：制备了五配位单核钴配合物[Co(TMC)Cl]ClO_4(**1**,TMC=1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane)。配合物 **1** 结晶于单斜晶系:$P2_1$,晶胞参数为 a=0.805 95(7) nm,b=1.486 58(12) nm,c=0.813 64(7) nm,β=110.190(2)°,V=0.914 93(13) nm^3,Z=2,T=120(2) K。钴与来自 TMC 配体的 4 个氮原子和 1 个氯离子配位,形成了扭曲的四方锥配位构型。磁性测试揭示了高自旋的钴离子具有场诱导的慢弛豫行为。

关键词：五配位；钴(Ⅱ)配合物；磁性能
中图分类号：O614.81+2　　**文献标识码**：A　　**文章编号**：1001-4861(2019)05-0914-05
DOI:10.11862/CJIC.2019.104

Crystal Structure and Magnetic Property of a Pentacoordinate Mononuclear Cobalt(Ⅱ) Complex

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Abstract: A pentacoordinate mononuclear cobalt(Ⅱ) complex, [Co(TMC)Cl]ClO_4 (**1**, TMC=1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane), is synthesized. It crystallizes in the monoclinic $P2_1$ with a=0.805 95(7) nm, b=1.486 58(12) nm, c=0.813 64(7) nm, β=110.190(2)°, V=0.914 93(13) nm^3, Z=2, T=120(2) K. The Co(Ⅱ) ion is coordinated to four N atoms from the TMC ligand and one Cl^- ion. The geometry of cobalt atom is best described as a distorted square pyramid. The magnetic measurements reveal the field induced slow relaxation behavior for the high-spin Co(Ⅱ) ion. CCDC: 1849513.

Keywords: pentacoordinate; cobalt(Ⅱ) complex; magnetic property

0 Introduction

Spin-crossover (SCO) complexes, as the bistable molecule-based materials, have attracted great attentions due to the promising applications in the field of molecular memory and switching. It is still challenging to design and synthesis a proper system which can show hysteretic SCO behavior near room temperature. The most commonly found SCO systems are based on the Fe(Ⅱ) and Fe(Ⅲ) ions[1]. However, only few reports of cobalt(Ⅱ) SCO systems were reported. The Co(Ⅱ) ion played an important role in magnetism among the all transition metals. The SCO cobalt(Ⅱ) complexes can also show two states, high-spin S=3/2 and low-spin S=1/2. The commonly found SCO Co systems are six-coordinated complexes[2]. Until now, five-coordinated Co(Ⅱ) systems are extremely rare[3].

Recently, Chen group reported the first example

收稿日期:2018-12-21。收修改稿日期:2019-03-07。
国家自然科学基金(No.21771200,21773316)资助项目。
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of SCO five-coordinate cobalt(Ⅱ) complex [Co(TMC)(CH_3CN)]X_2 (TMC=1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane)[4]. However, it exhibited an incomplete SCO property. The $\chi_M T$ value at 400 K was still smaller than the values expected for the high-spin state of Co(Ⅱ) ions, suggesting that the ligand field strength should be reduced for the five-coordinated Co(Ⅱ) complex. Considering the above mentioned facts, we chose the tetradentate ligand, TMC as the main ligand and adjusted the ligand field strength of the auxiliary ligand.

Herein, we report a pentacoordinate mononuclear cobalt(Ⅱ) complex, [Co(TMC)Cl]ClO_4, with four N atoms from the TMC ligand and one Cl^- ion from decomposition of $CHCl_3$. However, the ligand field of Cl^- ion is weak, which only produces the high spin state of Co(Ⅱ) ions in a temperature range of 2.5~300 K.

1 Experimental

All the reagents were commercially available and used as received. The FT-IR spectra were recorded in KBr tablets in the range of 4000~400 cm^{-1} on a PerkinElmer FT-IR spectrometer Frontier. The UV-Vis spectra were recorded in $BaSO_4$ in a range of 200~800 nm on UV-Vis-Nir Spectrophotometer UV-3600. The ESI-MS were recorded in MeOH in a range of m/z=50~800 on Liouid Chromatograph Mass Spectrometer LCMS-2010 A. The powder XRD patterns were recorded on a Rigaku Smartlab X-Ray diffractometer with Cu $K\alpha$ radiation (λ=0.154 178 nm, U=40 kV, I=26 mA) in a range of 5°~50° (2θ). The C, H and N microanalyses were performed for the dry crystals on an Elementar Vario-ELCHNS elemental analyzer. Magnetic susceptibility measurements for the sample were performed on a Quantum Design PPMS instrument operating under a field of 1 000 Oe. Diamagnetic correction was performed based on Pascal′ s coefficients.

1.1 Synthesis of [Co(TMC)Cl]ClO_4

1,4,7,10-tetraazacyclododecane (3 g, 17.4 mmol), HCOOH(98%~100%, 20 mL) and HCHO (37%, 5 mL) were mixed in 12 mL water. The solution was stirred and refluxed for 12 h at 105 ℃. The resulting solution was cooled in an ice bath and neutralized with KOH until pH=12. The TMC product was extracted with chloroform, and collected by rotary evaporation[5]. $Co(ClO_4)_2\cdot 6H_2O$ (3.15 g, 8.59 mmol) was dissolved in 15 mL MeCN. Then 15 mL acetonitrile solution of TMC containing 2 mL chloroform was added to this solution. The solution was stirred and refluxed for 12 h at 75 ℃. The violet crystalline product suitable for X-ray diffraction was collected by vacuum suction filtration, and finally washed with MeCN and MeOH. Yield: 40% (based on $Co(ClO_4)_2\cdot 6H_2O$). Anal. Calcd. for $C_{12}H_{28}Cl_2CoN_4O_4$(%): C, 34.14; H, 6.68; N, 13.27. Found(%): C, 34.44; H, 6.60; N, 13.17. IR (KBr, cm^{-1}): 3 118 (s), 2 930 (w), 2 880 (w), 2 830 (w), 1 661(w), 1 636(m), 1 478(m), 1 401(vs), 1 384(s), 1 298(m), 1 151(w), 1 101(s) and 1 084(vs), 1 023(m), 966(m), 912(m), 802(w), 755(m), 623(s), 585(w), 516(w), 473(w). UV-Vis ($BaSO_4$), λ_{max}/nm: 263, 365, 426, 520, 570, 600, 705. ESI-MS (CH_3OH): m/z=322.10 ([Co(TMC)(Cl)]$^+$).

1.2 Structure determination

Single-crystal diffraction data were recorded on a Bruker D8 QUEST diffractometer with Mo $K\alpha$ (λ=0.071 073 nm) radiation at 120 K. The crystal structure was solved by direct methods, and all non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL 2014/7 program[6]. Hydrogen atoms on organic ligands were generated by the riding mode. The responses to the alerts from checkCIF are quoted within the validation response form. The details of single-crystal diffraction data and selected bond lengths and bond angles are listed in Table 1 and 2, respectively.

CCDC: 1849513.

Table 1　Crystal structural data and refinement parameters for complex 1

Empirical formula	$C_{12}H_{28}Cl_2CoN_4O_4$	μ / mm^{-1}	1.253
Formula weight	422.21	F(000)	442
Crystal system	Monoclinic	Crystal size / mm	0.148×0.102×0.101
Space group	$P2_1$	2θ range for data collection / (°)	5.334~55.216

Continued Table 1

a / nm	0.805 95(7)	Reflection collected	18 342
b / nm	1.486 58(12)	Independent reflection	4 135 (R_{int}=0.038 6, R_σ=0.039 8)
c / nm	0.813 64(7)	Data, restraint, parameter	4 135, 13, 213
β / (°)	110.190(2)	Goodness-of-fit on F^2	1.116
Volume / nm^3	0.914 93(13)	Final R indexes [$I \geqslant 2\sigma(I)$]	R_1[a]=0.028 4, wR_2[b]=0.062 2
Z	2	Final R indexes [all data]	R_1=0.031 0, wR_2=0.063 1
D_c / (g·cm^{-3})	1.533		

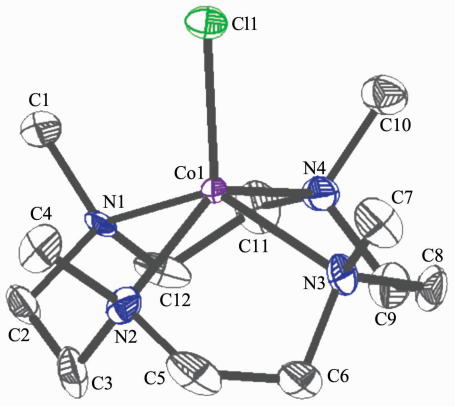
[a] $R_1=\sum||F_o|-|F_c||/\sum|F_o|$; [b] $wR_2=\{[\sum w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2 Selected bond lengths (nm) and bond angles (°) of complex 1

Co1-Cl1	0.226 15(10)	Co1-N2	0.214 2(4)	Co1-N4	0.213 5(3)
Co1-N1	0.216 8(3)	Co1-N3	0.217 8(3)		
N1-Co1-Cl1	109.98(9)	N3-Co1-Cl1	114.31(9)		
N2-Co1-Cl1	109.05(11)	N4-Co1-Cl1	115.64(10)		

2 Results and discussion

Complex **1** is obtained by reaction of the TMC and $Co(ClO_4)_2\cdot 6H_2O$ in acetonitrile and chloroform medium. The coordinated Cl^- ion maybe come from the decomposition of chloroform[7]. Complex **1** is characterized by single-crystal X-ray diffraction analysis. As shown in Fig.1, **1** is a mononuclear, five-coordinate Co(Ⅱ) complex. It crystallizes in the monoclinic space group of $P2_1$, containing one Co(Ⅱ)ion, one TMC and Cl^- ligand, and one ClO_4^- as counter anion in the asymmetric unit. The Co(Ⅱ) ion has a distorted square pyramidal coordination environment where four nitrogen donors from chelating TMC ligand form the basal plane, while the Cl^- ion occupies the apical position.



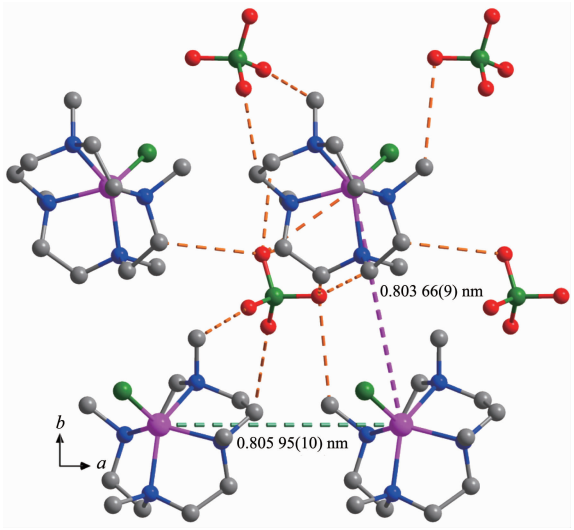
Thermal ellipsoids are drawn at the 30% probability; Hydrogen atoms are omitted for clarity

Fig.1 Molecular structure of **1**

The axial Co-Cl bond length is 0.226 2 nm, while the equatorial Co-N bond lengths are 0.213 5, 0.214 2, 0.216 8 and 0.217 8 nm. These bond lengths suggest a high-spin state of Co(Ⅱ) ion. The metal is deviated from the original N4 mean plane by ca. 0.081nm. Thus, the Cl-Co-N bond angles are deviated from 90° and fall in a range of 109.05°~115.64°. To further evaluate the degree of distortion, the Addison parameter ($\tau=(\alpha-\beta)/60$) is used, where α and β are the two largest basal angles[8]. Hence, the values of τ for the regular square pyramidal and trigonal bipyramidal geometries are 0 and 1, respectively. The calculated τ value is 0.006 for complex **1**, suggesting a slightly distorted square pyramidal geometry. It is also confirmed by the SHAPE 2.1 program, which gives a value of 0.834 with respect to ideal square pyramidal geometry[9].

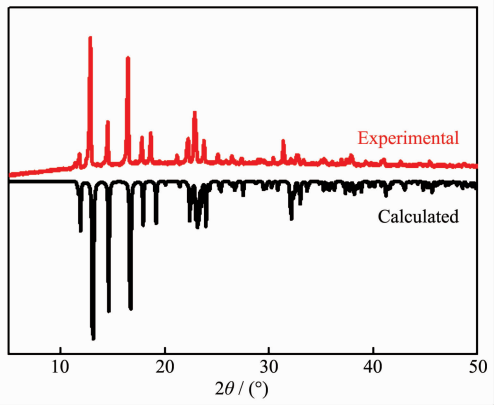
As shown in Fig.2, the $[Co(TMC)(Cl)]^+$ cations are linked with the ClO_4^- counter anions through very weak C–H···O interactions, in which the shortest C···O distance is 0.328 4 nm (C12···O4). The Co(Ⅱ) ions are effectively separated in **1** and the shortest Co···Co distance is 0.803 7 nm.

The phase purity of solid-state sample was demonstrated by elemental analysis and powered X-ray diffraction determination (Fig.3). The magnetic property of **1** was studied at 1 000 Oe in a temperature range



All hydrogen atoms were omitted for clarity; pink and sea green dash lines indicate the intermolecular Co···Co distances

Fig.2　View of a fragment of weak C–H···O interactions (orange dash line) in **1**



Simulated pattern is calculated from the crystal data at 120 K

Fig.3　Experimental PXRD pattern of complex **1** at room temperature

of 2.5~300 K. As shown in Fig.4a, the $\chi_M T$ value at 300 K was equal to 2.29 $cm^3 \cdot K \cdot mol^{-1}$, which was larger than the spin-only value (1.87 $cm^3 \cdot K \cdot mol^{-1}$) for a high-spin Co(Ⅱ) ion. It indicates the orbital contribution. When the temperature decreased to 100 K, the $\chi_M T$ value remained almost constant. Then, it gradually decreased to 1.44 $cm^3 \cdot K \cdot mol^{-1}$ at 2.5 K. Usually, the antiferromagnetic interaction and/or the thermal depopulation of the higher energy Kramers doublets of Co(Ⅱ) ion can contribute to the decrease of $\chi_M T$ at low temperature. Since the intermolecular Co···Co separations are larger, the possibility of any obvious magnetic interaction can be discarded. Therefore, the decline of the $\chi_M T$ value is mainly due to the intrinsic magnetic anisotropy of the Co(Ⅱ) ion.

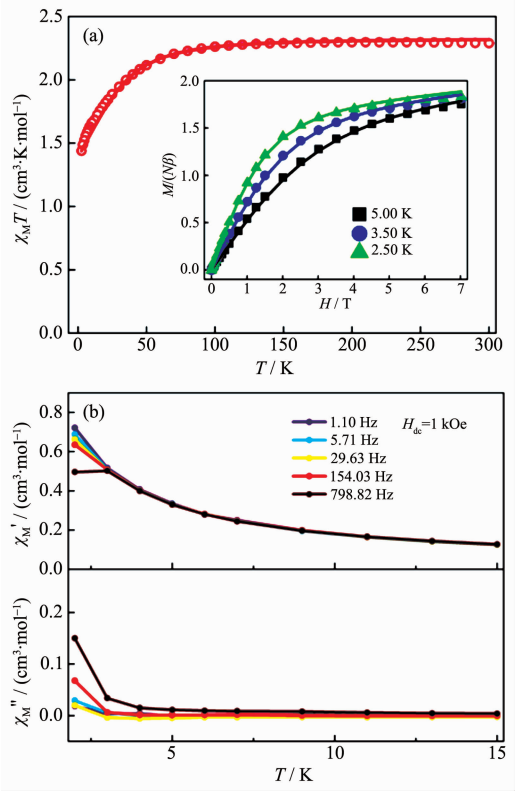


Fig.4　(a) Temperature dependence of $\chi_M T$ and field dependence of the magnetization (inset) for complex **1**; (b) ac magnetic susceptibility measurements under the applied field of 1 000 Oe

The field dependence of the magnetization for **1** was carried out at 2.50, 3.50 and 5.00 K in a field range of 0~7 T (Fig.4a inset). The magnetization at 7 T reached 1.83$N\beta$, which was lower than the theoretical saturation value (3.3$N\beta$) for Co(Ⅱ) ion with g=2.2. The lack of saturation and different isotherm magnetization plots suggest the presence of magnetic anisotropy in **1**.

In order to qualitatively estimate the anisotropy parameters, the magnetic data of **1** were analyzed with PHI program[10]. The spin Hamiltonian $\hat{H}=\mu_B g B\hat{S}+D\hat{O}_2^0$ (μ_B: Bohr magneton; g: isotropic g-factor; B: magnetic induction; $\hat{S}$: spin operator; D: axial zero-field splitting parameter; $\hat{O}_2^0$: Stevens operator; 2: tensor rank; 0: the component of tensor rank) was used. The best fit (Fig. 4) gave g=2.226±0.003, D=(−33.066±1.346) cm^{-1}. The

magnitude of axial anisotropy $|D|$= 33.066 cm^{-1} was comparable with other anisotropic five-coordinate Co(Ⅱ) complexes described in the literature[11].

To explore the dynamic magnetic behavior of **1**, alternating current (ac) magnetic susceptibility data was collected (Fig.4b). Unfortunately, the lack of out-of-phase signal (χ_M'') was observed under zero dc field. The appearance of frequency-dependence χ_M' and χ_M'' signals could occur after the application of external dc field of 1 000 Oe. However, no peaks could be observed. It suggests that the fast quantum tunneling of magnetization (QTM) can only be partially suppressed under non-zero dc field.

3 Conclusions

In conclusion, a pentacoordinate mononuclear cobalt(Ⅱ) complex with field induced slow magnetic relaxation behavior is reported. The Co(Ⅱ) ion is coordinated to four N atoms from the TMC ligand and one Cl^- ion, which can be described as a distorted square pyramid. The structural and magnetic data support the high-spin state for the Co(Ⅱ) ion. Therefore, to achieve a SCO pentacoordinate Co(Ⅱ) complex, suitable ligands with the ligand field stronger than Cl^- ion will be required.

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