

吡嗪酰腙席夫碱单核 Co(II)配合物的合成与磁性

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摘要: 合成了一个基于吡嗪酰腙席夫碱配体 H_2L 的单核 Co(II)配合物 $(NHEt_3)[Co(HL)_2] \cdot 3H_2O$ (**1**), 并通过红外光谱、热重分析、X射线单晶衍射分析及变温磁化率测定等对配合物进行了表征。X射线单晶衍射分析表明, 该配合物包含 1 个 Co(II)、2 个去质子化的 HL^- 配体以及未参与配位的 3 个水分子和 1 个质子化三乙胺, 中心 Co(II) 与 N_2O_4 六配位形成扭曲的八面体构型。配合物 **1** 以及去除水分子后的 **1** 的磁性测试表明二者均具有缓慢的高低自旋转换, 其不同之处归属为氢键对磁性的影响。

关键词: 酰腙配体; 单晶结构; 自旋转换; 单核钴配合物

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Synthesis and Magnetic Characterization of Mononuclear Co(II) Complex Based on Pyrazine-Containing Hydrazone Schiff Base Ligand

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Abstract: A mononuclear Co(II) complex $(NHEt_3)[Co(HL)_2] \cdot 3H_2O$ (**1**) based on a pyrazine-containing hydrazone Schiff base ligand H_2L was synthesized and characterized by IR, thermogravimetric analysis, X-ray single diffraction and magnetic susceptibility measurements. X-ray single crystal analysis reveals that it consists of a Co(II) ion, two deprotonated HL^- ligands, three uncoordinated H_2O and a protonated triethylamine. The central Co(II) ion is six-coordinated with N_2O_4 donor sets to form distorted octahedral geometry. Magnetic susceptibility measurement of both complex **1** and the dehydrated **1** showed a gradual high spin to low spin transition, and the differences can be attributed to the hydrogen bonding effects on the magnetic properties. CCDC: 1973542, **1** (298 K); 20274281, **1** (100 K).

Keywords: hydrazone ligand; single crystal structure; spin transition; mononuclear Co complex

0 Introduction

Spin - crossover (SCO) complexes have attracted much attention due to their promising applications in molecule-based memory devices, sensors and switches^[1-2]. Most of the work has focused on Fe(II)^[3-4] and Fe(III)^[5-6] complexes, there are still some mononuclear

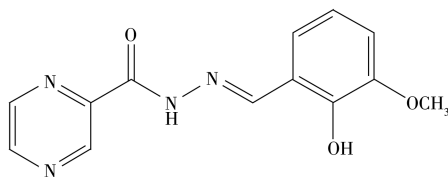
Co(II) complexes with abrupt or gradual SCO properties based on derivatives of terpyridine(terpy)^[7] and Schiff base ligands^[8]. The central Co(II) ion is coordinated by N_6 ^[9-10] and N_4O_2 donor sets^[11]. To the best of our knowledge, there are no reported Co(II) SCO complexes with N_2O_4 donor sets. The hydrazone Schiff base ligands have been well studied due to their ease of synthesis,

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modularity and various coordination modes with keto-enol tautomerism^[12]. Pyrazine-based hydrazone ligand H_2L as shown in Scheme 1 has been used to construct single-molecule magnets (SMMs) with rare earth metals^[13-17]. As a complementary work to this ligand system, herein, we synthesized a mononuclear Co(II) complex $(NH_4)_3[Co(HL)_2] \cdot 3H_2O$ (**1**) and characterized it with IR, thermogravimetric analysis (TGA), X-ray single diffraction and magnetic susceptibility.



Scheme 1 Structure of H_2L

1 Experimental

All chemical reagents were commercially available and used without further purification. H_2L was synthesized according to the reported method^[13]. FT-IR spectra were recorded in a range of 4 000~400 cm^{-1} on a PerkinElmer FT-IR spectrometer Frontier. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku Smartlab X-Ray diffractometer with Cu $K\alpha$ radiation ($\lambda=0.154\ 178\ nm$, $U=40\ kV$, $I=26\ mA$) in a range of $5^\circ\sim50^\circ$ (2θ). Elemental analyses for C, H and N were measured on an Elementar Vario MICRO analyzer. TGA curves were measured in a Al_2O_3 crucible using a PerkinElmer TGA instrument in a temperature range of $25\sim800\ ^\circ C$ under a N_2 flow at a heating rate of $20\ ^\circ C\cdot min^{-1}$. Magnetic susceptibility measurements for the samples were performed on the Quantum Design MPMS-XL instrument operating under a field of 1 000 Oe in a temperature range of $2\sim300\ K$.

1.1 Synthesis of $(NH_4)_3[Co(HL)_2] \cdot 3H_2O$ (**1**)

The methanol solution of $CoC_2O_4 \cdot 2H_2O$ (0.035 5 g, 0.20 mmol) was added dropwise to the mixed solution of H_2L (0.054 5 g, 0.20 mmol) in CH_3OH and CH_2Cl_2 with the addition of NEt_3 (5 drops) as a deprotonation reagent. The color of the mixture changed from yellow to brown slurring. After stirring for 6 h and the filtration, reddish brown filtrate was obtained. After slow evaporation of the filtrate for two weeks, needle like brown crystals were obtained for X-ray diffraction analysis. Yield: 52% (based on $CoC_2O_4 \cdot 2H_2O$). Anal. Calcd. for $C_{32}H_{43}CoN_9O_9$ (%): C, 50.79; H, 5.73; N, 16.66. Found(%): C, 51.36; H, 5.28; N, 17.27. IR (KBr, cm^{-1}): 3 431 (s), 2 934 (w), 2 831(w), 2 681 (w), 1 623(s), 1 600(s), 1 534(s), 1 475(s), 1 437(s), 1 345 (m), 1 243(w), 1 219(s), 1153(s), 1 083(m), 1 019(m), 976(m), 934(m), 858(w), 744(m), 643(w), 581(w), 453(w).

1.2 Structure determination

Single-crystal diffraction data were recorded on a Bruker SMART APEX II CCD diffractometer with Mo $K\alpha$ ($\lambda=0.071\ 073\ nm$) radiation at 298 K. The crystal structure was solved by direct methods and refined by full-matrix least-squares method on F^2 using the SHELXTL 2014/7 program and OLEX2^[18-19]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on water molecules were generated by the Q peaks. A water solvent molecule was severely disordered without adding hydrogen atoms and was modeled using the squeeze program. The details of single-crystal diffraction data and selected bond lengths and bond angles are listed in Table 1 and 2, respectively.

CCDC: 1973542, **1** (298 K); 20274281, **1** (100 K).

Table 1 Crystal data and structure refinement for complex **1**

Complex	1 (298 K)	1 (100 K)
Empirical formula	$C_{32}H_{43}CoN_9O_9$	$C_{32}H_{43}CoN_9O_9$
Formula weight	756.67	756.67
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a / nm	1.582 17(15)	1.576 9(6)
b / nm	1.015 77(10)	1.011 1(4)
c / nm	2.194 6(2)	2.171 7(8)

Continued Table 1

$\beta / (^{\circ})$	92.364(2)	92.914(7)
V / nm^3	3.524 0(6)	3.458(2)
Z	4	4
$D_e / (\text{g} \cdot \text{cm}^{-3})$	1.426	1.454
μ / mm^{-1}	0.549	0.564
$F(000)$	1 548	1 580
θ range / $(^{\circ})$	2.217~25.027	2.223~23.828
Reflection collected, unique	17 474, 6 225 ($R_{\text{int}}=0.051$)	17 008, 6 077
Data, restraint, parameter	6 225, 39, 469	6 077, 12, 474
Final R indices [$I > 2\sigma(I)$]	$R_1=0.066\ 3$, $wR_2=0.163\ 4$	$R_1=0.073\ 6$, $wR_2=0.176\ 6$
R indices (all data)	$R_1=0.106\ 1$, $wR_2=0.186\ 7$	$R_1=0.119\ 8$, $wR_2=0.199\ 8$
Goodness of fit on F^2	1.024	1.043

Table 2 Selected bond lengths (nm) and angles ($^{\circ}$) for complex **1**

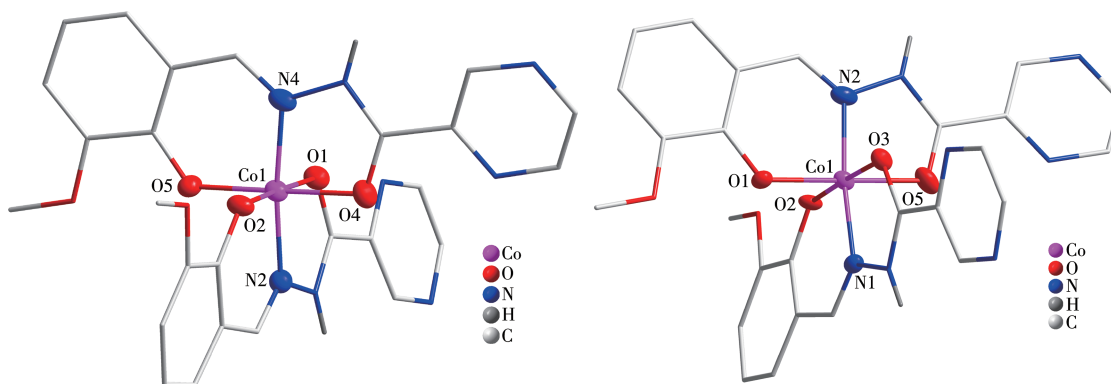
1 (298 K)					
Co(1)—O(1)	0.190 8(3)	Co(1)—O(2)	0.188 4(3)	Co(1)—O(4)	0.189 7(3)
Co(1)—O(5)	0.188 1(3)	Co(1)—N(2)	0.186 4(3)	Co(1)—N(4)	0.185 7(4)
O(2)—Co(1)—O(1)	177.32(14)	O(2)—Co(1)—O(4)	89.71(14)	O(4)—Co(1)—O(1)	87.82(14)
O(5)—Co(1)—O(1)	90.91(13)	O(5)—Co(1)—O(2)	91.58(13)	O(5)—Co(1)—O(4)	178.60(13)
N(2)—Co(1)—O(1)	83.24(14)	N(2)—Co(1)—O(2)	95.80(14)	N(2)—Co(1)—O(4)	91.20(15)
N(2)—Co(1)—O(5)	89.22(14)	N(4)—Co(1)—O(1)	92.39(14)	N(4)—Co(1)—O(2)	88.34(14)
N(4)—Co(1)—O(4)	83.70(16)	N(4)—Co(1)—O(5)	95.78(15)	N(4)—Co(1)—N(2)	173.43(17)
1 (100 K)					
Co(1)—O(1)	0.188 7(3)	Co(1)—O(2)	0.188 5(3)	Co(1)—O(3)	0.190 7(3)
Co(1)—O(5)	0.189 9(4)	Co(1)—N(1)	0.186 6(4)	Co(1)—N(2)	0.186 7(4)
O(1)—Co(1)—O(3)	91.16(15)	O(1)—Co(1)—O(4)	179.14(16)	O(2)—Co(1)—O(1)	91.39(15)
O(2)—Co(1)—O(3)	177.26(15)	O(2)—Co(1)—O(5)	89.46(15)	O(5)—Co(1)—O(3)	87.99(15)
N(1)—Co(1)—O(1)	88.80(16)	N(1)—Co(1)—O(2)	95.52(16)	N(1)—Co(1)—O(3)	83.52(16)
N(1)—Co(1)—O(5)	91.21(17)	N(1)—Co(1)—N(2)	173.35(19)	N(2)—Co(1)—O(1)	96.40(17)
N(2)—Co(1)—O(2)	88.51(16)	N(2)—Co(1)—O(3)	92.21(17)	N(2)—Co(1)—O(5)	83.53(18)

2 Results and discussion

2.1 Crystal structure

Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in monoclinic system, space group $P2_1/c$. The coordination environment of Co(II) in **1** is shown in Fig.1. It consists of a Co(II) ion, two deprotonated HL[−], one protonated NEt₃ and three free H₂O molecules. The central Co(II) is coordinated by two nitrogen atoms and four oxygen atoms from HL[−]. There could be amido-enol tautomerism in one HL[−] ligand and the enol was deprotonated in order to balance the charge of the

complex. The Co(II) ion has a distorted octahedral coordination geometry where four oxygen donors form the basal plane, and the two nitrogen donors occupy the apical position. The distortion parameter, Σ , is defined as the sum of the deviation from the 12 *cis*-O—Co—O, N—Co—O, N—Co—N angles^[1]. The smaller Σ value of 35.63 $^{\circ}$ for **1** shows a slightly distorted octahedral geometry. The Co—N bond lengths (Co1—N2 0.186 4(3) nm, Co1—N4 0.185 7(4) nm) are slightly shorter than the reported Co complex with N₂O₄ donor sets. While the Co—O bond lengths (Co1—O1 0.190 8(3) nm, Co1—O2 0.188 4(3) nm, Co1—O4



Solvent molecules and all hydrogen atoms have been omitted except NH group for clarity

Fig.1 Coordination environment of Co(II) ion in complex **1** (left: 298 K, right: 100 K) with 50% probability thermal ellipsoids

0.189 7(4) nm, Co1—O5 0.188 1(3) nm) are comparable to the reported Co complex^[20]. We also determined the crystal structure of **1** at 100 K as shown in Fig.1, it reveals the same structure composition and coordination environment of the central Co ion. The bond lengths of Co—O and Co—N are slightly different with **1** at 298 K. The Σ value of 37.29° also shows a slightly distorted octahedral geometry. The free water molecules form O—H···O hydrogen bonds with O from phenol and methoxy group as shown in Fig.2. There are also O—H···N hydrogen bonds with N from pyrazine N and N atom from the protonated triethylamine.

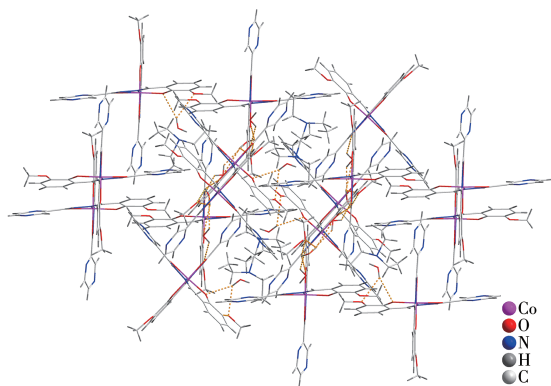


Fig.2 Packing structure of complex **1** (298 K) with hydrogen bonding

2.2 PXRD patterns and TGA analysis

PXRD pattern of the complex was determined at room temperature to check the phase purity as shown in Fig.3. The peak positions of the experimental PXRD match well with the simulated one, indicating the purity of the complex.

TGA of **1** was carried out in a range of 25~800 °C

under nitrogen atmosphere. As shown in Fig.4, the first weight loss of 6.9% from 95 to 185 °C is attributed to the loss of free H₂O molecules (Calcd. 6.89%). The second weight loss of 13.1% from 195 to 260 °C is attributed to the loss of one protonated NEt₃ (Calcd. 13.7%). After that, the complex began to decompose.

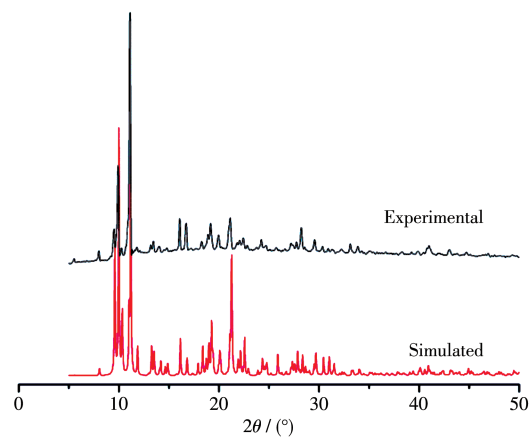


Fig.3 PXRD patterns for **1**

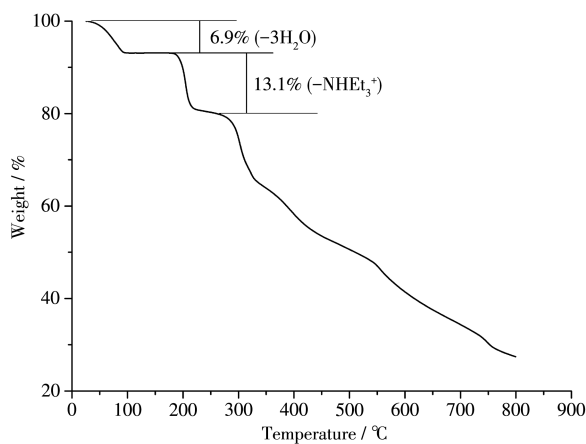
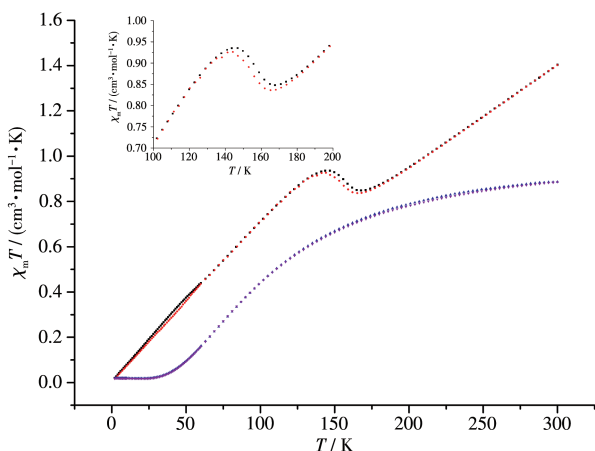


Fig.4 TGA curve of **1**

2.3 Magnetic analysis of complex **1** and dehydrated **1**

The magnetic susceptibilities χ_m of **1** and dehydrated **1** were measured in the 2~300 K temperature range. The $\chi_m T$ versus T plots for both in cooling and heating mode are shown in Fig. 5. The $\chi_m T$ value of $1.40 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ was lower than the theoretical value of $1.88 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ of the high-spin mononuclear Co(II), indicating a mixture of high-spin and low-spin state. The $\chi_m T$ decreased gradually as the temperature lowered. It reached $0.848 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at about 168 K, then it began to increase slowly to $0.935 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 147 K, indicating a slightly reverse spin transition due to possible phase changes during this period of temperature range^[21-23]. This was confirmed by the slightly different bond lengths and the Σ value for complex **1** at 298 K and 100 K. The $\chi_m T$ was $0.44 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 59 K corresponding to the mononuclear Co(II) low-spin state, and it decreased with decreasing temperature until it reached about $0.02 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 2 K, there was a small hysteresis loop in the cooling and heating mode as shown in Fig. 5. In order to check the solvent effects on the magnetic properties, the dehydrated complex **1** was obtained by annealing **1** at 115 °C for 6 h *in vacuo*. The $\chi_m T$ value of $0.89 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ for dehydrated **1** was significantly lower than the theoretical value of $1.88 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ of the high-spin mononuclear Co(II), indicating a majority of low-



Inset: "reverse" fragment of the curve around 150 K

Fig.5 $\chi_m T$ vs T plots for complex **1** (cooling: black, heating: red) and dehydrated **1** (cooling: blue, heating: pink) in cooling and heating mode

spin state. The $\chi_m T$ decreased gradually as the temperature lowered. It reached $0.43 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at about 78 K corresponding to the mononuclear Co(II) low-spin state. It also kept decreasing to *ca.* $0.02 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 2 K, and no hysteresis loop was observed in the cooling and heating mode. The difference of **1** and the dehydrated **1** can be assigned as the hydrogen bonding effects on the magnetic properties^[24].

3 Conclusions

In summary, we have successfully synthesized and characterized a new mononuclear Co(II) complex based on a pyrazine-containing hydrazone Schiff base ligand with rare N_2O_4 donor sets. The complex **1** exhibited a gradual spin transition with an unusual reverse spin state transition due to possible phase changes. The dehydrated **1** also showed a gradual spin transition, and the differences can be assigned as the hydrogen bonding effects on the magnetic properties.

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