第 30 卷第 1 期
2014 年 1 月

无 机 化 学 学 报
CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol.30 No.1
149-154

1-氢-1,2,3-三氮唑-4,5-二甲酸构筑的六核钴配合物：合成、晶体结构和磁性

邹吉勇[1,2] 师 唯*,[1] 高洪苓[2] 崔建中[2] 程 鹏*,[1]

([1]南开大学化学系,先进能源材料化学教育部重点实验室,天津化学化工协同创新中心,天津 300071)

([2]天津大学化学系,天津 300072)

摘要：以 1-氢-1,2,3-三氮唑-4,5-二甲酸为配体合成了 1 个六核钴配合物,$[Co_6(TDA)_4(H_2O)_{14}]\cdot 5H_2O$ (**1**)(H_3TDA=1*H*-1,2,3-triazole-4,5-dicarboxylic acid)。对其进行了红外光谱、元素分析、热重分析、X-射线单晶和粉末衍射表征。晶体结构分析表明该配合物属于正交晶系,$P2_12_12$ 空间群,晶胞参数:*a*=1.647 30(2) nm,*b*=1.653 30(2) nm,*c*=0.726 90(10) nm,Flack 参数为 0.00(13)。配合物中 6 个钴离子通过 4 个 1-氢-1,2,3-三氮唑-4,5-二甲酸桥联成 1 个六核钴单元,六核钴单元之间进一步通过氢键连成三维超分子结构。磁性测试表明钴离子之间存在反铁磁相互作用。

关键词：1-氢-1,2,3-三氮唑-4,5-二甲酸；六核钴单元；晶体结构；反铁磁相互作用

中图分类号：O614.81+2 **文献标识码**：A **文章编号**：1001-4861(2014)01-0149-06

DOI:10.11862/CJIC.2014.085

A Hexanuclear Co^{II} Complex Assembled with 1H-1,2,3-Triazole-4,5-dicarboxylic Acid: Synthesis, Crystal Structure and Magnetic Property

ZOU Ji-Yong[1,2] SHI Wei*,[1] GAO Hong-Ling[2] CUI Jian-Zhong[2] CHENG Peng*,[1]

([1]*Department of Chemistry, Key Laboratory of Advanced Energy Materials Chemistry (MOE), and Synergetic Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin* 300071, *China*)

([2]*Department of Chemistry, Tianjin University, Tianjin* 300072, *China*)

Abstract: A new hexanuclear Co^{II} complex, namely $[Co_6(TDA)_4(H_2O)_{14}]\cdot 5H_2O$ (**1**) (H_3TDA=1*H*-1,2,3-triazole-4,5-dicarboxylic acid), has been successfully synthesized and characterized by infrared spectra, elemental analysis, thermogravimetric analysis, powder and single-crystal X-ray diffraction. Complex **1** crystallizes in orthorhombic space group $P2_12_12$, with cell parameters: *a*=1.647 30(2) nm, *b*=1.653 30(2) nm, *c*=0.7326 90(10) nm and Flack parameter of 0.00(13). In title complex, six Co^{II} ions are connected by four TDA^{3-} ligands to form a hexanuclear Co^{II} unit, which can be extended to a 3D supramolecular architecture through the hydrogen-bonding interactions. Magnetic study reveals the dominant antiferromagnetic interaction exist between Co^{II} ions in **1**. CCDC: 930110.

Key words: 1*H*-1,2,3-triazole-4,5-dicarboxylic acid; hexanuclear Co^{II} unit; crystal structure; antiferromagnetic interaction

0 Introduction

The exploration of molecular magnetic materials assembled with paramagnetic metal centers and multidentate organic ligands with the aid of crystal engineering is one of the most current objectives in chemistry and materials science due to their potential applications in the fields of high-density data storage

收稿日期:2013-09-30。收修改稿日期:2013-12-12。

国家自然科学基金(No.21331003),教育部博士点基金(No.20120031130001),天津市自然科学基金(No.13JCZDJC32200)资助项目。

*通讯联系人。E-mail:pcheng@nankai.edu.cn

devices, nanosized electronics and quantum information processing[1-4]. Among them, polynuclear complexes were given considerable attention because they exhibit attractive magnetic properties such as in single-molecule magnets[5-7], as well as the understanding of the rules between the macroscale classical properties and the microscale quantum properties[8-9]. However, it is still a challenge to synthesize high-nuclearity complexes in a rational way because of the difficulties in precise controlling over the nuclearity of the complexes during the assembly process.

In order to construct polynuclear metal complexes, the selection of appropriate ligands with special coordination symmetry is essential. We have focused on 1*H*-1,2,3-triazole-4,5-dicarboxylic acid (H_3TDA) as ligand due to (i) its diverse coordination modes to afford various structures[10-16], (ii) its special coordination symmetry with triangular secondary building units (SBUs), and (iii) its superexchange capacity in interesting magnetic properties[11-16]. Although various complexes based on 1*H*-1,2,3-triazole-4,5-dicarboxylic acid have been reported, most of them are Mn^{II}-based complexes. The investigations on Co^{II}-based complexes assembled by 1*H*-1,2,3-triazole-4,5-dicarboxylic acid as magnetic materials are still limited[11,15].

In this contribution, a new hexanuclear Co^{II} complex, namely $[Co_6(TDA)_4(H_2O)_{14}]\cdot 5H_2O$ (**1**), has been successfully obtained and structurally characterized in detail. The title hexanuclear Co^{II} complex can be connected with each other through the hydrogen-bonding interactions to build a 3D supramolecular architecture. Magnetic study has been performed as well.

1 Experimental

1.1 Materials and physical measurements

H_3TDA was prepared according to literature[17]. Other reagents and solvents were purchased from commercial sources and used as received without further purification. Elemental analysis for C, H and N were performed on a Perkin-Elmer 240 CHN elemental analyzer. IR spectrum was recorded in the range 400 ~4 000 cm^{-1} with a Bruker Tensor 27 Spectrometer on KBr disks. Powder X-ray diffraction measurement was recorded on a D/Max-2500 X-ray diffractometer using Cu $K\alpha$ radiation. Thermogravimetric analysis (TGA) was carried out on a Delta Series TA-SDTQ 600 in nitrogen atmosphere from room temperature to 800 ℃ (10 ℃·min^{-1}) using aluminum crucibles. Magnetic susceptibility measurement was performed on a Quantum Design SQUID MPMS VSM magnetometer. Diamagnetic correction was made with Pascal′s constants.

1.2 Synthesis

A mixture of H_3TDA (0.1 mmol, 0.015 7 g), HTZ (0.1 mmol, 0.006 9 g) (HTZ=1*H*-1,2,4-triazole) and $Co(OAc)_2\cdot 4H_2O$ (0.15 mmol, 0.037 4 g) was dissolved in H_2O (6 mL). The mixture was sealed in a 25 mL Teflon-lined stainless steel reactor heated at 90 ℃ for 72 h, and subsequently cooled to room temperature at a rate of 0.8 ℃·h^{-1}. Red rhombus crystals of **1** in *ca.* 10% yield (based on Co) were collected. Anal. Calcd. for $C_{16}H_{38}N_{12}O_{35}Co_6$(%): C 14.64, H 2.92, N 12.81. Found(%): C 14.48, H 3.05, N 12.56. IR (KBr, cm^{-1}): 3 399(vs), 2 921(s), 2 851(m), 1 716(m), 1 551(vs), 1 372(s), 1 221(w), 1 031(w), 783(w), 659(w).

1.3 Crystallographic studies

Data collection of **1** was performed on an Oxford Supernova diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.071 073 nm). The structure was solved by direct methods using the SHELXS-97 programs[18]. All non-hydrogen atoms were refined by full-matrix least-squares techniques on F^2 using the SHELXL-97 programs. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms of H9a, H9b, H10a, H10b, H11a, H11b, H12a, H12b, H13a, H13b, H14a, H14b, H15a and H15b were placed in idealized positions and those of H16a, H16b, H17a, H17b and H18 were located in the difference Fourier map. The crystallographic data for **1** are listed in Table 1 and the selected hydrogen bonding interactions in complex **1** are shown in Table 2.

CCDC: 930110.

Table 1　Crystal data and structure refinements for 1

Complex	**1**	Flack parameter	0.00(13)
Formula	$C_{16}H_{38}N_{12}O_{35}Co_6$	D_c / (g·cm^{-3})	2.18
Formula weight	1 312.16	μ / mm^{-1}	2.57
Crystal system	Orthorhombic	F(000)	1 316
Space group	$P2_12_12$	Reflections collected / unique	25 057 / 3 527
a / nm	1.647 30(2)	GOF on F^2	1.065
b / nm	1.653 30(2)	R_{int}	0.037 9
c / nm	0.732 690(10)	R_1, wR_2 ($I>\sigma(I)$)	0.029 3, 0.073 9
V / nm^3	1.995 47(4)	R_1, wR_2 (all data)	0.033 5, 0.075 1
Z	2	Residues / (e·nm^{-3})	1 231 / −452

Table 2　Selected hydrogen bonding interactions in complex 1

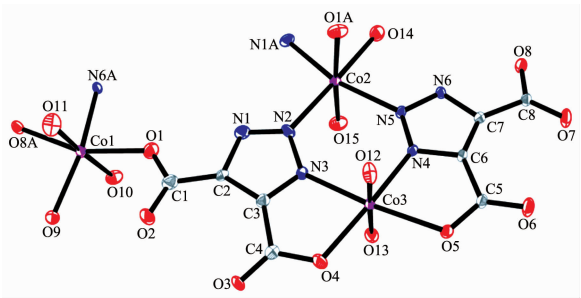
D–H···A	d(D-H) / nm	d(H···A) / nm	d(D···A) / nm	∠DHA / (°)
O9–H9a···O12B	0.085 3	0.195 7	0.276 6	157.97
O10–H10a···O5A	0.085 0	0.214 0	0.284 2	139.80
O10–H10a···O13A	0.085 0	0.253 1	0.324 9	142.64
O11–H11b···O5B	0.085 2	0.210 1	0.290 7	157.85
O11–H11a···O15C	0.084 5	0.235 0	0.315 2	158.86
O12–H12a···O17D	0.084 5	0.194 1	0.275 0	160.58
O13–H13b···O7A	0.084 2	0.198 9	0.281 0	164.27
O14–H14a···O17D	0.084 4	0.197 1	0.280 1	169.65
O15–H15b···O16	0.084 7	0.267 4	0.268 7	152.72
O17–H17a···O3B	0.086 0	0.189 5	0.266 5	148.31
O17–H17b···O15C	0.085 1	0.231 4	0.303 0	141.94
O18–H18···O4	0.085 1	0.191 9	0.268 9	149.86

Symmetry codes: A: −1/2−x, 1/2+y, −1−z; B: −1/2−x, 1/2+y, −2−z; C: −x, −y, z; D: x, y, 1+z.

2　Results and discussion

2.1　Description of crystal structure

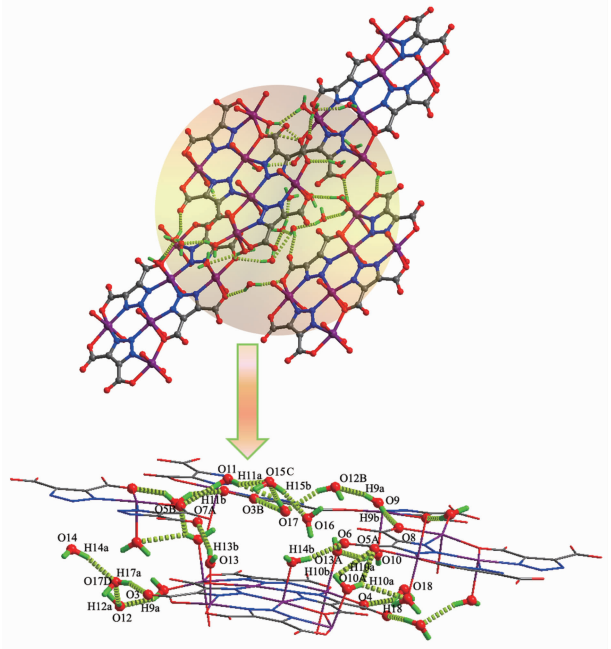
Single crystal X-ray diffraction study reveals that **1** crystallizes in the orthorhombic space group $P2_12_12$. Each unit cell contains crystallographically independent three Co^{Ⅱ} ions, two TDA^{3-} ligands, seven coordinated water molecules, two and a half lattice water molecules (Fig.1). Co1, Co2 and Co3 ions adopt similar coordination environments. Co1 adopts a slightly distorted octahedral {CoO_5N} coordination geometry with two oxygen atoms (O1 and O8A) and one nitrogen atom (N6A) from two TDA^{3-}, three oxygen atoms (O9, O10 and O11) from three water molecules. The bond lengths of Co1-O are in the range of 0.203 6 (4)~0.218 5(3) nm and that of Co1-N is 0.203 6 (3) nm, respectively. Co2 adopts a distorted octahedral {CoO_3N_3} coordination geometry with one oxygen atom (O1A) and three nitrogen atoms (N1A, N2 and N5) from three TDA^{3-}, two oxygen atoms (O14 and O15) from two water molecules. The bond lengths of Co2-O and Co2-N are in the range of 0.207 0(3)~0.219 8(3) nm and 0.206 2(4)~0.214 6(4) nm, respectively. The coordination geometry of Co3 is an octahedral {CoO_4N_2} configuration with two oxygen atoms (O4 and O5) and two nitrogen atoms



Symmetry code: A: −x, −y, z

Fig.1　ORTEP drawing of **1** showing the local coordination environments of the Co^{Ⅱ} ions with 30% thermal ellipsoids

(N3 and N4) from two TDA^{3-}, two oxygen atoms (O12 and O13) from two water molecules. The bond lengths of Co3-O and Co3-N are in the range of 0.205 7(3)~0.219 6(3) nm and 0.200 9(3)~0.206 4(3) nm, respectively. There are two different types of TDA^{3-} ligands: one chelates two Co^{II} ions (Co3 and Co2A) through the carboxylate oxygen atoms (O1 and O4) and the triazole nitrogen atoms (N1 and N3), one crystallographically equivalent Co2 ion through the same triazole nitrogen atom N2 neighboring to N1 atom and another Co1 ion through the same oxygen atom (O1) from one μ_2-η_1:η_1 carboxylate. Whereas the other one chelates two Co^{II} ions (Co3 and Co1A) through the carboxylate oxygen atoms (O5 and O8) and the triazole nitrogen atoms (N4 and N6), and bridges another Co2 ion through the same triazole nitrogen atom N5 neighboring to N4 atom. In this case, six Co^{II} ions are simultaneously coordinated by four TDA^{3-} ligands to form a hexanuclear Co^{II} unit, which can be extended to a 3D supramolecular architecture through the hydrogen-bonding interactions (Fig.2). It is well known that H_3TDA is more readily to construct the high-dimensional complexes because of their special coordination modes[10-15]. The studies of the discrete high-nuclearity complexes with 1*H*-1,2,3-triazole-4,5-dicarboxylic acid are still rare and only one example of such tetranuclear complex could be found in recent literature[19], which is obtained with the help of a terminal ligand. Therefore, the title complex is the highest-nuclearity discrete complex constructed by 1*H*-1,2,3-triazole-4,5-dicarboxylic acid as far as we know.



Some hydrogen atoms were omitted for clearity;. Purple: Co; red: O; blue: N; black: C, green: H; Symmetry codes: A: −1/2−*x*, 1/2+*y*, −1−*z*; B: −1/2−*x*, 1/2+*y*, −2−*z*; C: −*x*, −*y*, *z*; D: *x*, *y*, 1+*z*

Fig.2 3D supramolecular architecture formed by hydrogen-bonding interactions in **1**

2.2 XRPD pattern and thermal stability

To confirm the crystalline phase purity of **1**, the XRPD experiment has been carried out at room temperature. The diffraction peaks of bulk sample **1** are consistent with the simulated patterns in terms of the single crystal data, indicating the presence of mainly one crystalline phase (Fig.3). To confirm the thermal stability of **1**, the TGA has been studied under N_2 atmosphere (Fig.4). The TGA curve shows the weight loss of 25.91% for **1** are in the range from

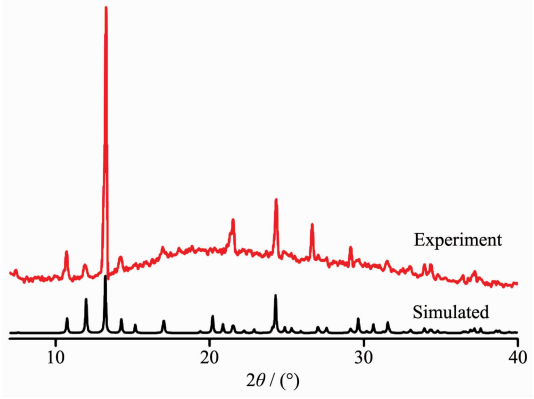


Fig.3 Comparison of the experimental PXRD pattern of as-synthesized **1** with the one simulated from its single crystal structure

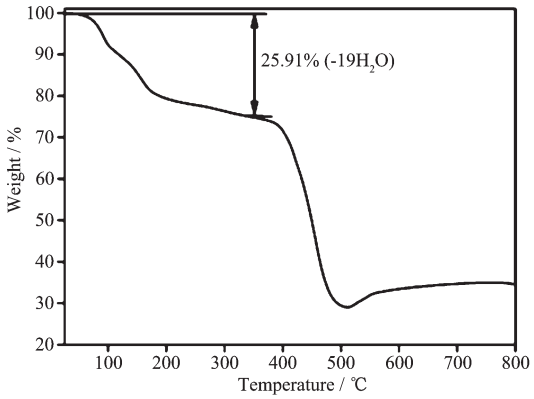
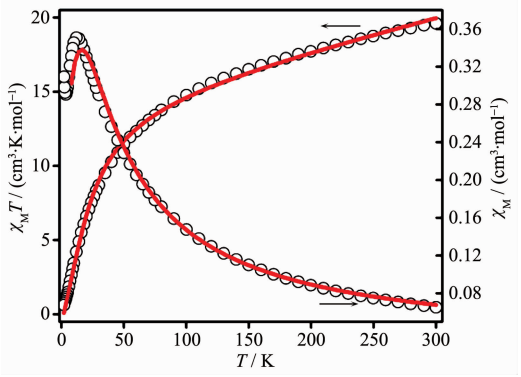


Fig.4 Thermal gravimetric analysis of **1**

25 to 320 ℃, corresponding to the removal of five uncoordinated water molecules and fourteen coordinated water molecules. After the losses of all water molecules, no weight loss is observed, indicating the decomposition of **1**.

2.3 Magnetic properties

The temperature dependence of the magnetic susceptibility of **1** was measured in an applied direct-current (dc) magnetic field of 1 kOe in the temperature range of 2~300 K. As shown in Fig.5, the $\chi_M T$ value at room temperature is 19.61 $cm^3 \cdot K \cdot mol^{-1}$, which is much higher than the expected spin-only value of 11.28 $cm^3 \cdot K \cdot mol^{-1}$ for six high-spin Co^{II} ions in an octahedral coordination environment because of the unquenched orbital-moment[20-21]. Upon cooling, the $\chi_M T$ value drops gradually to 0.62 $cm^3 \cdot K \cdot mol^{-1}$ at 2 K. In the plot of χ_M-T, a maximum at 12 K is observed, indicative of antiferromagnetic interactions between the magnetic centers. The increase of χ_M below 3.5 K implies the presence of the paramagnetic impurities in **1**. The fitting by Curie-Weiss law with the data above 20 K gives C=22.40 $cm^3 \cdot K \cdot mol^{-1}$ and θ=−49.45 K. The large and negative Weiss constant may arise from the antiferromagnetic interactions and/or spin-orbit coupling effect of the Co^{II} ions. To roughly analyze the magnetic interaction in such Co^{II} complex with orbital contribution, the data can be fitted by the expression of eq **1**~**2**[22-24], in which TIP is the temperature-independent paramagnetism of the Co^{II} ion. The best fit using a least-squares analysis lead to J=−3.66 cm^{-1}, g=2.27, TIP=0.003 4 $cm^3 \cdot mol^{-1}$ and R=7.91×10^{-4}. The fitting result indicates the existence of weak antiferromagnetic interaction between the Co^{II} ions in **1** and the spin-orbital coupling contributes to the trivial g factor[23-24].



Red line denotes the theoretical curve with the best-fit parameters

Fig.5 Temperature dependence of magnetic susceptibility for **1** in 2~300 K at 1 kOe field

$$\chi=\frac{Ng^2\beta}{kT}\frac{14+5X^6+X^{10}}{7+5X^6+3X^{10}+X^{12}}+\mathrm{TIP} \quad (1)$$

$$X=e^{\frac{-J}{KT}} \quad (2)$$

In summary, a new hexanuclear Co^{II} complex assembled by 1*H*-1,2,3-triazole-4,5-dicarboxylic acid has been successfully obtained and structurally studied. Complex **1** is a hexanuclear Co^{II} unit, which can be further connected through the hydrogen-bonding interactions to build a 3D supramolecular architecture. Magnetic study reveals dominant antiferromagnetic exchange interactions exist between Co^{II} ions in **1**. This work illustrates a rational way for the construction of polynuclear molecular magnetic materials with the help of multi-chelating ligands. Further systematic studies for the design and construction with this ligand are still underway in our laboratory.

Reference:

[1] Gatteschi D, Sessoli R, Villain J. *Molecular Nanomagnets*. New York: Oxford University Press, **2006**.

[2] Kahn O. *Molecular Magnetism*. Weinheim: VCH, **1993**.

[3] Miller J S. *Chem. Soc. Rev.*, **2011**,**40**:3266-3296

[4] Bogani L, Wernsdorfer W. *Nat. Mater.*, **2008**,**7**:179-186

[5] Wang Y X, Shi W, Cheng P, et al. *Chem. Sci.*, **2012**,**3**:3366-3370

[6] Mondal K C, Sundt A, Powell A K, et al. *Angew. Chem. Int. Ed.*, **2012**,**51**:7550-7554

[7] Hill S, Edwards R S, Christou G, et al. *Science*, **2003**,**302**:1015-1018

[8] Leng J D, Liu J L, Tong M L. *Chem. Commun.*, **2012**,**48**:5286-5288

[9] Liu T, Zhang Y J, Gao S, et al. *J. Am. Chem. Soc.*, **2008**, **130**:10500-10501

[10]Zou J Y, Cui J Z, Cheng P, et al. *CrystEngComm*, **2013**,**15**:2682-2687

[11]Zou J Y, Shi W, Cheng P, et al. *Chem. Commun.*, **2013**,**49**:8226-8228

[12]Zou J Y, Shi W, Cheng P, et al. *RSC Adv.*, **2013**,**3**:21511

-21516

[13]Zou J Y, Shi W, Cheng P, et al. *Eur. J. Inorg. Chem.*, **2013**, DOI:10.1002/ejic.201301312

[14]Shi W, Chen X Y, Cheng P, et al. *Eur. J. Inorg. Chem.*, **2006**:4931-4937

[15]Zhang W X, Xue W, Chen X M, et al. *CrystEngComm*, **2008**,**10**:1770-1776

[16]Zhang W X, Xue W, Chen X M, et al. *Chem. Commun.*, **2009**:3804-3806

[17]Hinlel L E, Richards G O, Thomas O. *J. Chem. Soc.*, **1937**: 1432-1437

[18]Sheldrick M. *Acta Cryst.*, **2008**,**A64**:112-122

[19]Wang S, Eddaoudi M, Liu Y L, et al. *J. Am. Chem. Soc.*, **2010**,**132**:18038-18041

[20]Carlin E L. *Magnetochemistry*. Berlin: Springer-Verlag, **1986**.

[21]Xiong K C, Jiang F L, Hong M C, et al. *Chem. Sci.*, **2012**,**3**: 2321-2325

[22]Yang L, Jin W, Lin J. *Polyhedron*, **2000**,**9**:93-98

[23]Liu Y H, Tsai H L, Lu K L. *Inorg. Chem.*, **2001**,**40**:6426-6431

[24]Zhang S Y, Shi W, Cheng P, et al. *Dalton Trans.*, **2011**,**40**: 7993-8002