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Low temperature heat capacity and magnetic property of two H_2ZTO-Co(II) coordination polymers (H_2ZTO = 4,4′-azo-1,2,4-triazol-5-one)

Sheng Zhang [a,b,1], Xiaxia Song [a,1], Guowei Lin [a], Qi Yang [a,*], Quan Shi [c,*], Hui Zheng [c], Xin Liu [c], Qing Wei [a], Gang Xie [a], Sanping Chen [a,*], Shengli Gao [a]

[a] Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an, Shaanxi 710069, China
[b] College of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Baoji 721013, China
[c] Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

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ABSTRACT

In this paper, two new H_2ZTO-Co(II) coordination polymers (H_2ZTO = 4,4′-azo-1,2,4-triazol-5-one), $[Co(H_2ZTO)_2(H_2O)_4](NO_3)_2$ (1) and $\{[Co(H_2ZTO)(H_2O)_4](NO_3)_2{\cdot}2H_2O\}_n$ (2), have been synthesized and characterized. Polymer **2** is derived from **1** and undergoes a multistage transformation by soaking **1** in distilled water. X-ray single crystal structure analyses showed that **2** exhibit a one-dimensional (1D) chain geometry coordinated by 0D units of **1** through uncoordinated nitrogen atoms of H_2ZTO ligands. The thermal decomposition behaviors and magnetic properties of **1** and **2** were discussed. In addition, the low-temperature (1.9–300 K) heat capacities of **1** and **2** were measured using the heat capacity option of a Quantum Design Physical Property Measurement System (PPMS). The thermodynamic functions of **1** in the experimental temperature range were derived by fitting the heat capacity data to a series of theoretical and empirical models. Using the fitted heat capacity results, the standard molar entropy and standard molar enthalpy have been respectively calculated to be (871.1 ± 8.7) $J{\cdot}mol^{-1}{\cdot}K^{-1}$ and (132.7 ± 1.3) $kJ{\cdot}mol^{-1}$ for **1**.

1. Introduction

In the past decades, many efforts have been concentrated on the rational design and synthesis of transition-metal coordination polymers (TMCPs) due to their intriguing architectures and topologies as well as potential versatile applications as functional materials [1–7]. As one kind of multifunctional material, triazole-based TMCPs have been intensively studied in the fields of magnetism, luminescence, catalysis, gas storage and separation in recent years owing to their unique physical and chemical properties associated with the easy modification of their molecular structures [8–12].

The heat-capacity calorimetry is a very useful tool to investigate thermal properties of crystalline materials among various thermodynamic measurements at low temperature [13–15] because heat capacity is a bulk measurement [16]. Furthermore, heat capacity extremely sensitive to crystallographic and magnetic phase transitions, leading to insight regarding long- and short-range ordering and the nature of the ordering. However, although the magnetic properties and magneto-structural correlations of TMCPs have been widely explored [17–19], to our knowledge, low temperature heat capacity about such magnetic materials has been rarely reported [20,21].

As part of our continuous efforts towards new functional triazole-based TMCPs [22,23], in this work, 4,4′-azo-1,2,4-triazol-5-one (H_2ZTO) is selected as ligand to assemble with Co(II) ion under ambient conditions, aiming at the construction of new TMCPs and the further investigation of their low temperature heat capacity and magnetic property. Herein, we report the syntheses, crystal structures, thermal decomposition behaviors of two new H_2ZTO-Co(II) coordination polymers, $[Co(H_2ZTO)_2(H_2O)_4](NO_3)_2$ (1) and $\{[Co(H_2ZTO)(H_2O)_4](NO_3)_2{\cdot}2H_2O\}_n$ (2). In particular, polymer **1** undergoes a multistage transformation to yield **2** in aqueous solution. **2** exhibits a one-dimensional (1D) chain geometry coordinated by 0D units of **1** through uncoordinated nitrogen atoms of H_2ZTO ligands. Additionally, the magnetic properties of **1** and **2** and the low temperature heat capacity of **1** were discussed in detail.

* Corresponding authors.
E-mail addresses: yangqi@nwu.edu.cn (Q. Yang), shiquan@dicp.ac.cn (Q. Shi), sanpingchen@nwu.edu.cn (S. Chen).
[1] These authors have equal contribution to this work.

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2. Experimental

2.1. Materials, equipments and analytical methods

All chemicals involved were acquired from commercial sources at analytical grade and used without further purification, detailed information is provided in Table 1. Elemental analysis (C, H, N) was implemented on a Perkin-Elmer 2400 CHN elemental analyzer. The content of metal Co was assayed by EDTA titration method. The FT-IR spectra were recorded in the range of 400–4000 cm^{-1} using KBr pellets on an EQUINOX55 FT/IR spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a Netzsch STA 449C instrument and a CDR-4P thermal analyzer of Shanghai Balance Instrument factory, respectively, using nitrogen atmosphere at a flow rate of 10 mL min^{-1}. About 0.8 mg samples were put into the aluminium pan, a temperature range of 323–723 K and a heating rate of 10 K min^{-1} were used for both DSC and TG measurements. To determine the repeatability of DSC and TG measurements, using polymer **1** as samples, seven times DSC and TG experiments were repeated respectively (Seen in Fig. S1, Tables S1 and S2). The results show that the repeatability of DSC and TG measurements are ±0.6 K and ±0.8 K, respectively. The single crystal X-ray experiments were performed on a Rigaku SCX mini CCD diffractometer equipped with graphite-monochromatized Mo Kα radiation (λ = 0.071073 nm) using ω and φ scan mode. The data integration and reduction were processed with SAINT software. Absorption correction based on multiscan was performed using the SADABS program. [24] The structures were solved by the direct method using SHELXTL and refined by means of full-matrix least-squares procedures on F^2 with SHELXL-97 program. [25] All nonhydrogen atoms were refined anisotropically. Magnetic measurements were accomplished on crystalline samples (25.11 mg for **1**, 22.25 mg for **2**) using a Quantum Design MPMS-XL7 SQUID magnetometer at temperatures between 2 K and 300 K for direct current (dc) applied fields with the applied field of 1000 A/m (restrained in eicosane to prevent torqueing at high fields). The measured susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables). Powder X-ray diffraction (PXRD) measurements executed on a RU 200 diffractometer (Rigaku) at 60 kV and 300 mA, using Cu Kα radiation (λ = 0.15406 nm) (Fig. S2†).

The heat capacity measurements were performed using a Quantum Design PPMS in zero magnetic field with logarithmic spacing over the temperature range from 1.9 to 100 K and at 10 K intervals from 100 to 300 K. The accuracy of the heat capacity measurements on a high-purity copper pellet and α-Al_2O_3 cylinder (SRM720) was found to be ±2% and ±1% in the temperature ranges from 1.9 to 20 K and from 20 to 300 K, respectively [26]. The crystalline samples were measured according to a PPMS heat capacity measurement technique developed by Shi et al. [27,28] and the accuracy of this technique was verified to be ±3% and ±1% in the temperature ranges below 20 K and from 20 to 300 K, respectively, by measuring a powdered benzoic acid sample (SRM 39j) using PPMS. The details of the sample preparation and the heat capacity experimental procedure can be found in related publications [27,28]. In general, sample preparation consisted of mixing the sample with copper strips in a copper cup, which was then compressed into a pellet using a stainless steel die. The copper cup was formed from a 0.025 mm thick pure copper foil, with a mass fraction purity of 0.99999, while the pellet had a 2.8 mm diameter and height of 3.5 mm. A typical heat capacity measurement involved two steps: the heat capacity measurement of the addenda of the PPMS platform with Apiezon N was first decided as $C_{addenda}$, and then the heat capacity of the pellet consisting of the sample, the copper strips, and the copper cup was measured as C_{total}. Thus, the heat capacities for the samples were calculated by subtracting $C_{addenda}$ from C_{total}, and consequently the heat capacity of the samples can be obtained by subtracting the copper heat capacity from the pellet heat capacity. Using the PPMS technique, the heat capacities of crystalline samples of 10.25 mg for **1** and 14.01 mg for **2** were respectively measured over the temperature range of 1.9–300 K.

2.2. Synthesis and characterization

2.2.1. Synthesis of $[Co(H_2ZTO)_2(H_2O)_4](NO_3)_2$ (1)

$Co(NO_3)\cdot 6H_2O$ (0.2 mmol, 0.0584 g) was dissolved in the mixture of 8 cm^3 concentrated nitric acid and H_2ZTO (0.1 mmol, 0.0196 g). After stirring for 1 h in air, the filtrate was allowed to evaporate slowly at room temperature. Orange block crystals were obtained after 10 days (Yield 65%, based on Co^{2+}). Anal. Calcd for $CoC_8H_{16}N_{18}O_{14}$ (647.32): C, 14.85; H, 2.49; N, 38.95; Co, 9.11%. Found: C, 14.90; H, 2.50; N, 38.91; Co, 9.05%. IR data (KBr, cm^{-1}): 3457(vs), 3340(vs), 3223(vs), 3095(s), 2931(s), 2755(s), 2475(m), 2358(m), 2112(w), 2019(w), 1739(vs), 1669(s), 1610(m), 1563(s), 1434(vs), 1364(vs), 1271(s), 1224(vs), 1049(m), 932(s), 874(m), 722(s), 593(s) (Fig. S3†).

2.2.2. Synthesis of $\{[Co(H_2ZTO)(H_2O)_4](NO_3)_2\cdot 2H_2O\}_n$ (2)

The crystals of **1** were soaked into distilled water and yielded perfect red block crystals of **2** after 6 days at room temperature. Anal. Calcd for $CoC_4H_{16}N_{10}O_{14}$ (487.20): C, 9.86; H, 3.31; N, 28.75; Co, 12.10%. Found: C, 9.88; H, 3.34; N, 28.82; Co, 12.18%. IR data (KBr, cm^{-1}): 3462(vs), 3219(vs), 3145(s), 3089(vs), 2942(s), 2747(s), 2478(m), 2421(w), 2356(m), 2152(w), 2121(w), 2015(w), 1746(vs), 1665(vs), 1608(m), 1560(s), 1437(vs), 1364(vs), 1323(vs), 1226(vs), 1055(m), 941(s), 876(m), 819(s), 714(s), 592(s) (Fig. S3†).

3. Results and discussion

3.1. Description of crystal structures

The details of crystal data, data collection parameters, and refinement statistics of polymers **1** and **2** are given in Table 2. The selected bond lengths and bond angles are listed in Tables S3 and S4† in Supporting Information.

Table 1
Provenance and mass fraction purity of chemicals used in this study.

Chemical name	Source of supply	Mass fraction purity	Purification method
$Co(NO_3)\cdot 6H_2O$	Aladdin Reagent Co., Ltd, China	≥0.995[a]	None
H_2ZTO	Aladdin Reagent Co., Ltd, China	≥0.99[a]	None
Nitric acid	Xi'an Chemical Reagent Factory, China	≥0.68[a]	None
Absolute ethanol	Xi'an Chemical Reagent Factory, China	≥0.998[a]	None
Polymer **1**	Synthesis	≥0.993[b]	Solvent washing (absolute ethanol)
Polymer **2**	Synthesis	≥0.991[b]	Solvent washing (absolute ethanol)

[a] As stated by the supplier.
[b] Evaluated by the measured contents of C, H, N and Co.