

## NOTE

### Solvothermal Synthesis and Crystal Structure of Nickel Cluster Based on Benzotriazole

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A novel nickel cluster  $[\text{Ni}_9(\text{btz})_{12}(\text{CH}_3\text{COO})_6(\text{DMA})_6]$  (**1**;  $\text{btz}$  = 1H-benzotriazole;  $\text{DMA}$  = *N,N*-dimethylacetamide) has been solvothermally prepared and structurally characterized by single-crystal X-ray diffraction, which shows that this compound crystallized in the hexagonal space group P-3 with  $a = 22.199(5)$  Å,  $b = 22.199(5)$  Å,  $c = 24.696(5)$  Å,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ ,  $V = 10540(4)$  Å<sup>3</sup>,  $Z = 3$ .

**Key Words:** Solvothermal synthesis, Crystal Structure, Nickel, Benzotriazole.

A 1H-benzotriazole ligand has been used as building block for constructing a functional supramolecular architecture in the crystal engineering<sup>1</sup>. And then another auxiliary ligands acting as connector linked these building blocks resulting in 2D or 3D frameworks. In the course of this work, we have prepared an intriguing nickel cluster based on 1H-benzotriazole.

All commercially available reagents and solvents purchased were used without further purification. Thermal stability studies were carried out on a NETSCHZ STA-449C simultaneous TG-DSC thermoanalyzer with a heating rate of  $15^\circ\text{C min}^{-1}$  in  $\text{N}_2$  atmosphere. X-ray powder diffraction patterns of  $[\text{Ni}_9(\text{btz})_{12}(\text{CH}_3\text{COO})_6(\text{DMA})_6]$  (**1**) were collected on a MiniFlex-II diffractometer.

**Preparation of compound:** The synthesis of  $[\text{Ni}_9(\text{btz})_{12}(\text{CH}_3\text{COO})_6(\text{DMA})_6]$  was performed out in 23 mL Teflon-lined stainless steel containers under autogenous pressure. A mixture of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.1010 g, 0.35 mmol), pyrazine (0.0306 g, 0.37 mmol), 1H-benzotriazole ( $\text{btz}$ , 0.0681 g, 0.57 mmol), D-camphoric acid (0.0306 g, 0.16 mmol), methanol (2.5 mL) and *N,N*-dimethylacetamide ( $\text{DMA}$ , 7.5 mL) in a Teflon flask was placed in a steel bomb. The bomb was placed in an oven maintained at  $100^\circ\text{C}$  for 5 days and then cooled to room temperature. The green crystals were filtered off, washed with ethanol and then air-dried.

**X-crystallography:** Suitable single crystals of **1**  $[\text{Ni}_9(\text{btz})_{12}(\text{CH}_3\text{COO})_6(\text{DMA})_6]$  were carefully selected under an optical microscope and glued to thin glass fibers. Whereafter, single-crystal X-ray diffraction analyses were performed on a computer-controlled XCalibur E CCD diffractometer with graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda_{\text{MoK}\alpha} = 0.71073$  Å)

at  $T = 293.2$  K. Empirical absorption corrections were made using the SADABS program<sup>2</sup>. The structures were solved using the direct method and refined by full-matrix least-squares methods on  $F^2$  by using the SHELX-97 program package<sup>3</sup>. All non-hydrogen atoms were refined anisotropically and hydrogen atoms attached to carbon or nitrogen atoms were fixed at their ideal positions.

**Structure description:** Single-crystal X-ray diffraction shows that compound **1** crystallized in space group P-3. The asymmetric unit of compound **1** consists of three independent Ni atoms, five 1H-benzotriazole ligands, one deprotonated acetic acid ligands from the decomposition of dimethylacetamide solvent *in situ* and one dimethylacetamide molecules. As shown in Fig. 1a, although all Ni centers are same six-coordinate, their coordination environments are different. Both Ni1 and Ni2 is bonded by six nitrogen atoms from two 1H-benzotriazole ligands with the Ni-N bond lengths in the range from 2.053(19) Å to 2.161(16) Å and the N-Ni-N bond angles range from  $88.5(7)^\circ$  to  $180.0(11)^\circ$ . While Ni3 is six coordinated by three nitrogen atoms from one 1H-benzotriazole ligands with the Ni3-N bond lengths in the range from 2.004(17) Å to 2.11(2) Å, three oxygen atoms from one chelating carboxylate groups of one deprotonated acetic acid ligand and one DMA molecules with the Ni3-O bond lengths in the range from 2.100(15) Å to 2.195(17) Å and the O-Ni3-O bond angles range from  $64.1(7)^\circ$  to  $80.2(7)^\circ$ . In the structure of **1**, Ni1 locates at a special site with a symmetry center, so that other symmetry-related Ni2 and Ni3 center are generated and construct a nine-nuclear Ni cluster (Fig. 1b).

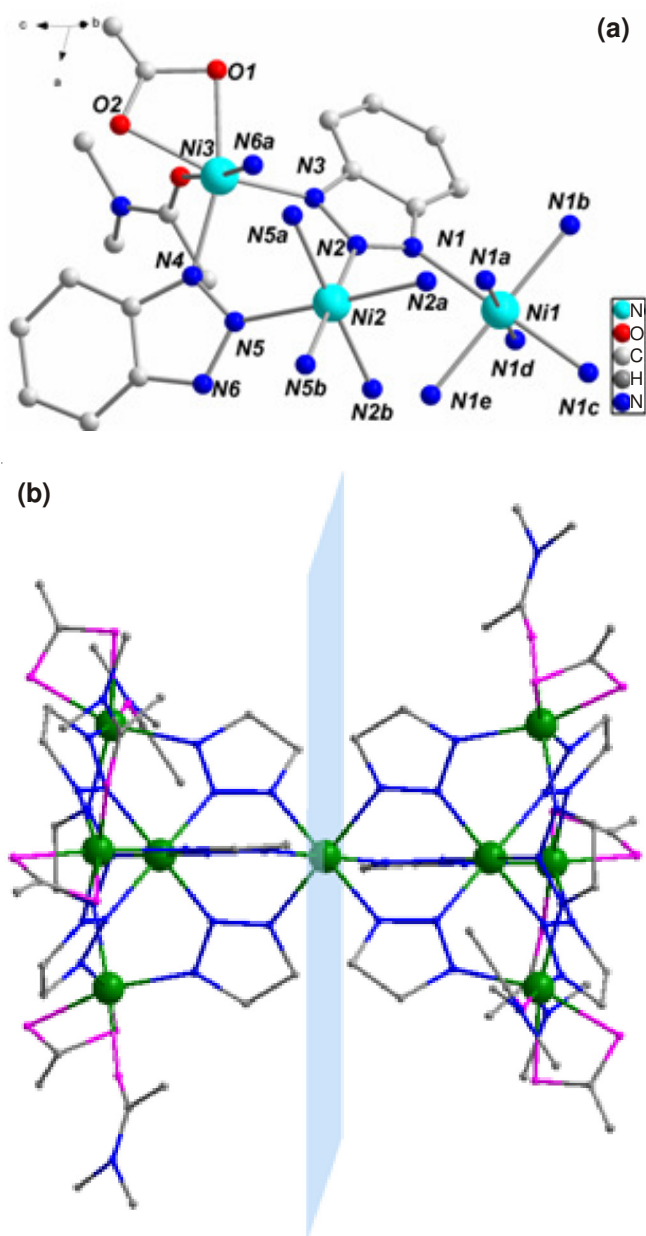


Fig. 1. (a) the coordination environment around the Ni atoms in  $[\text{Ni}_9(\text{btz})_{12}(\text{CH}_3\text{COO})_6(\text{DMA})_6]$ ; (b) perspective view of nine-nuclear Ni cluster of  $[\text{Ni}_9(\text{btz})_{12}(\text{CH}_3\text{COO})_6(\text{DMA})_6]$ . Hydrogen atoms are omitted and 1,2,3-1H-triazole represent 1H-benzotriazole for clarity

**Thermogravimetric analysis:** The phase purity of compound **1** was confirmed by similarities between its simulated and experimental powder X-ray diffraction (Fig. 2a). To evaluate the thermal behaviour, the thermal behaviour of compound **1** was analyzed on a crystalline sample under a nitrogen atmosphere from 30 to 640 °C at a heating rate of 10 °C min<sup>-1</sup> (Fig. 2b). The thermogravimetric curve of compound **1** has two

distinct steps of weight loss. The first weight loss of 27.59 % from 30 to 270 °C corresponds to the loss of two coordinated DMA molecules and deprotonated acetic acid ligands (calcd. 29.56 %). After loss of coordinated DMA molecules and acetate ligands, the second weight loss is due to the decomposition of the 1H-benzotriazole ligands over 330 °C, accompanying the collapse of the whole framework.

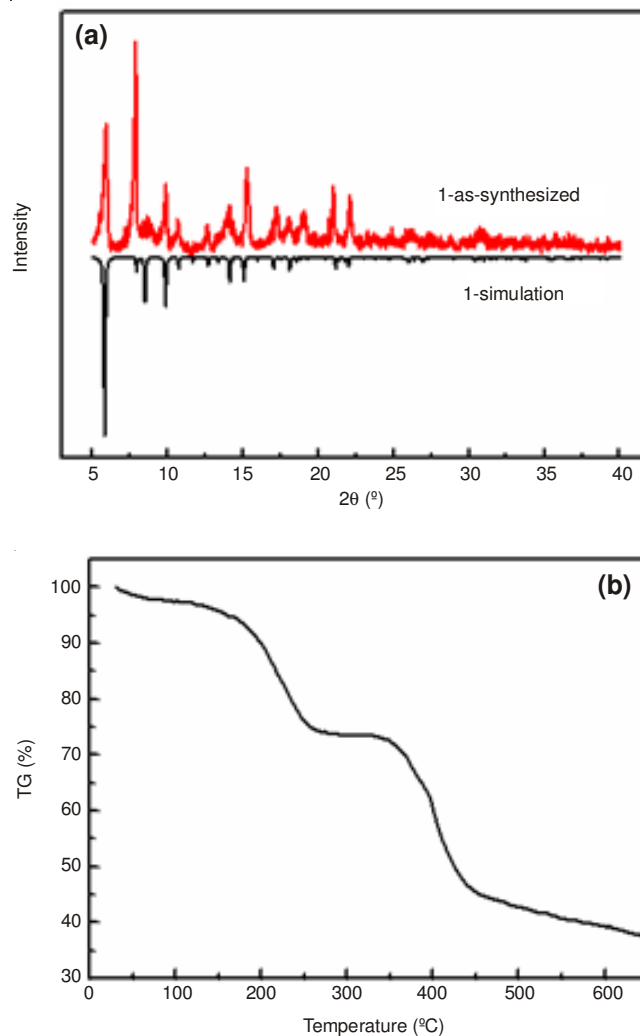


Fig. 2. (a) Characterization of bulk phase of  $[\text{Ni}_9(\text{btz})_{12}(\text{CH}_3\text{COO})_6(\text{DMA})_6]$  by XRD; (b) the TGA plots of  $[\text{Ni}_9(\text{btz})_{12}(\text{CH}_3\text{COO})_6(\text{DMA})_6]$

## REFERENCES

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