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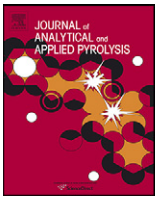

Solid state synthesis, thermodynamics and catalytic combustion effect of a high energy nickel(II) coordination compound

Qi Yang[a], Qing Wei[a], San-Ping Chen[a,*], Guo-Chun Zhang[a,b], Chun-Sheng Zhou[a,b], Sheng-Li Gao[a,b]

[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] *Department of Chemistry and Chemical Engineering, Shaanxi Key Laboratory of Comprehensive Utilization of Tailing Resources, Shangluo University, Shangluo 726000, China*

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ABSTRACT

Self-assembly of Ni(II) with 3,5-diamino-1,2,4-triazole resulted in a 3D supramolecular compound $[Ni_3(Hdatrz)_6(fma)_2(H_2O)_4]fma\cdot 11H_2O$ (**1**) in the presence of coligand fumaric acid (Hdatrz = 3,5-diamino-1,2,4-triazole, H_2fma = fumaric acid). X-ray structural analysis reveals that three nickel ions are bridged by six neutral Hdatrz ligands, and abundant lattice water molecules exist in **1**. Based on the structural framework and TG curve of **1**, a new energetic compound $[Ni_3(Hdatrz)_6(fma)_2(H_2O)_4]fma$ (**2**) with 35.5% of nitrogen content was readily prepared through dehydration of **1** at 398 K under N_2 atmosphere. The enthalpy change of the reaction of formation for **1** was determined to be $(-23.24 \pm 0.05)\ \mathrm{kJ\ mol^{-1}}$ by microcalorimetry at (298.15 ± 0.01) K. Thermodynamic and thermokinetic parameters k, E, n, $\Delta S^{\theta}_{\neq}$, $\Delta H^{\theta}_{\neq}$ and $\Delta G^{\theta}_{\neq}$ of the reaction of formation for **1** were obtained. Thermoanalytical kinetics of the reaction of formation for **2** was further investigated. The sensitivity experiment results indicated that **2** was more sensitive to impact and friction stimuli that **1**. As an additive, **2** effectively promoted the thermal decomposition of ammonium perchlorate (AP), which projected the potential application of the compound **2** as combustion modifier in solid propellants.

1. Introduction

Development of energetic materials with high energy, high heat resistance and low sensitivity is a major goal in the area of high energy materials (HEMs) [1]. Recently, considerable attention has been paid to metal coordination compounds with high-nitrogen heterocyclic groups because of their flexible structures and favorable energetic properties [2–8]. As polydentate building blocks, 1,2,4-triazole and its derivatives combine the coordination geometries of both pyrazoles and imidazoles, exhibiting an extensively documented ability to bridge metal ions to afford polynuclear clusters [9]. More practically, 1,2,4-triazole and its derivatives are excellent energy components of energetic materials [10,11].

Ammonium perchlorate (AP) is the common oxidizer in composite solid propellants. The thermal decomposition characteristic of AP directly influenced the combustion behaviors of solid propellants [12]. Many combustion catalysts reported on the thermal decomposition of AP, such as metal oxides, were of no energetic compounds [13–17].

Our research group were currently interested in the synthesis, the energy and sensitivity characteristics of the polymeric transition metal compounds with 1,2,4-triazole or its derivatives and carboxylates as coligands [18,19]. We anticipate these compounds would work as excellent promoter for the thermal decomposition of AP.

Herein, we firstly synthesized compound $[Ni_3(Hdatrz)_6(fma)_2(H_2O)_4]fma\cdot 11H_2O$ (**1**) with 3,5-diamino-1,2,4-triazole as ligand in the presence of coligand fumaric acid. X-ray diffraction single crystal analysis revealed that abundant free water molecules occurred in **1**. TG curve showed that **1** was dehydrated at 498 K. Inspired by the TG result, a nitrogen-rich compound **2** was secondly prepared through dehydration of **1** at 498 K in tubular oven under N_2 atmosphere, which was identified as a formula $[Ni_3(Hdatrz)_6(fma)_2(H_2O)_4]fma$ by chemical analysis and PXRD. The enthalpy change of the reaction of formation for **1** at (298.15 ± 0.01) K was determined by mirocalorimetry, and thermodynamics and thermokinetics of the reaction of formation were investigated. Furthermore, the reaction of formation for **2** was elucidated from the viewpoint of thermoanalytical kinetics. In order to evaluate the safety and the catalytic combustion effect of **2**, the sensitivity and the catalytic performance toward thermal decomposition of AP were explored.

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* Corresponding author.
E-mail address: sanpingchen@126.com (S.-P. Chen).

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2. Experimental

2.1. Materials and instruments

All reagents used were purchased from commercial sources and used without further purification.

C, H and N analyses were carried out using an instrument of Vario EL III CHNOS of Germany. The precision of the elemental analysis was within 5‰. Infrared (IR) spectra drawn at regular intervals were recorded on a Bruker FTIR instrument as KBr pellets. TG-DTG analysis was conducted on a P.E. 2100 company thermal analyzer under N_2 atmosphere from room temperature to 873 K. ICP-AES experiment was carried out on a T.E. IRIS advantage inductively coupled plasma atomic emission spectrophotometer. The calorimetric experiments were performed with an RD496-CK2000 Microcalorimeter (Southwest Institute of Electron Engineering, China) [20]. The calorimetric constant at (298.15 ± 0.01) K was determined by the Joule effect to be (63.901 ± 0.030) $\mu V\,mW^{-1}$. The enthalpy of dissolution of KCl (spectral purity) in deionized water was measured to be (17.246 ± 0.004) $kJ\,mol^{-1}$, which was in good agreement with the reported value of (17.241 ± 0.018) $kJ\,mol^{-1}$ [21]. The sensitivity to impact stimuli was determined by the standard staircase method applying fall hammer apparatus with a 2 kg drop weight. The results were reported in terms of height for 50% probability of explosion ($h_{50\%}$) [22]. The friction sensitivity was determined on a Julius Peter's apparatus by following the BAM method [23].

2.2. Synthesis

Synthesis of the precursor compound $[Ni_3(Hdatrz)_6(fma)_2(H_2O)_4]fma\cdot 11H_2O$ (**1**): a solution of $NiCl_2\cdot 6H_2O$ (0.1 mmol, 0.024 g) in 8 cm^3 H_2O was slowly added to the mixture solution of Hdatrz (0.2 mmol, 0.020 g) in 8 cm^3 H_2O and H_2fma (0.1 mmol, 0.012 g) in 8 cm^3 H_2O with continuous stirring. Upon being filtered, the filtrate was kept undisturbed at room temperature for 3 days. Green single crystals suitable for X-ray analysis were obtained. Anal. Calcd. $C_{24}H_{74}N_{30}Ni_3O_{27}$ weight (%): C, 20.72; H, 5.36; N, 30.21. Found: C, 20.68; H, 5.30; N, 30.29. Yield: 40%. IR (KBr, cm^{-1}): 3425(s), 1622(s), 1588(s), 1448(s) and 1340(s).

Synthesis of the compound $[Ni_3(Hdatrz)_6(fma)_2(H_2O)_4]fma$ (**2**): the compound **1** was put into a drying tubular oven and kept heating at 398 K for half an hour under N_2 atmosphere. Pale green powders were obtained. Anal. Calcd. $C_{24}H_{44}N_{30}Ni_3O_{16}$ weight (%): C, 24.33; H, 3.74; N, 35.46. Found: C, 24.57; H, 3.83; N, 35.82. IR (KBr, cm^{-1}): 1620(s), 1585(s), 1445(s) and 1342(s).

2.3. X-ray crystallography

The single crystal X-ray experiment was performed on a Bruker Smart Apex CCD diffractometer equipped with graphite monochromatized Mo Kα radiation (λ = 0.071073 nm) using ω and φ scan mode. The single-crystal structure of compound was solved by direct methods and refined with full-matrix least-squares refinements based on F^2 using SHELXS 97 and SHELXL 97 [24,25]. All non-H atoms were located using subsequent Fourier-difference methods. In all cases hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms. Crystal data and refinement details are summarized in Table 1. Selected bond distances and bond angles are given in Table 2.

Table 1
Crystal data and structure refinement parameters for compound **1**.

Empirical formula	$C_{24}H_{66}N_{30}Ni_3O_{27}$
Formula weight	1383.14
Crystal system	Triclinic
Space group	*P*−1
a (nm)	1.0122(3)
b (nm)	1.1795(3)
c (nm)	1.3423(3)
α (°)	68.978(4)
β (°)	69.295(4)
γ (°)	70.286(5)
V (nm^3)	1.3580(6)
Z	1
F(0 0 0)	722
$D_{calc.}$ ($g\,cm^{-3}$)	1.694
μ (mm^{-1})	1.141
Reflections collected	6887
T_{max}/T_{min}	0.8566/0.7259
Data/restraint/param	4735/16/401
Goodness-of-fit on F^2	1.014
Final *R* indices	$R_1 = 0.0631$
[*I* > 2sigma(*I*)]	$wR_2 = 0.1572$
R indices (all data)	$R_1 = 0.1081$
	$wR_2 = 0.1948$
Largest peak and hole ($e\,nm^{-3}$)	762 and −755

Table 2
Selected bond lengths (nm) and bond angles (°) for compound **1**.

Ni(1)—N(11)	0.2060(6)	Ni(1)—N(10)	0.2119(5)
Ni(1)—N(4)	0.2142(5)	Ni(2)—N(12)	0.2057(6)
Ni(2)—N(5)	0.2063(6)	Ni(2)—N(9)	0.2073(5)
Ni(2)—O(1)	0.2114(5)	Ni(2)—O(2)	0.2081(5)
Ni(2)—O(3)	0.2115(4)		
N(11)—Ni(1)—N(10)	91.60(2)	N(11)—Ni(1)—N(4)	91.90(2)
N(10)—Ni(1)—N(4)	91.00(2)	N(12)—Ni(2)—N(5)	93.80(2)
N(5)—Ni(2)—O(1)	175.20(2)	N(5)—Ni(2)—O(2)	92.70(2)
N(5)—Ni(2)—O(3)	90.20(2)	N(9)—Ni(2)—O(1)	87.40(2)
N(9)—Ni(2)—O(2)	176.10(2)	O(2)—Ni(2)—O(1)	89.50(2)
N(12)—Ni(2)—O(3)	174.40(2)	N(12)—Ni(2)—O(1)	90.60(2)

3. Results and discussion

3.1. Structure of the precursor **1**

The single-crystal analysis reveals that the precursor **1** consists of one linear trinuclear cation, one discrete fma^{2-} anion and eleven lattice water molecules (Fig. 1). In the trinuclear cation, three nickel ions are bridged by six neutral Hdatrz ligands. The central nickel ion is located at the inversion center, exhibiting a distorted octahedron geometry afforded by six nitrogen atoms from six Hdatrz ligands.

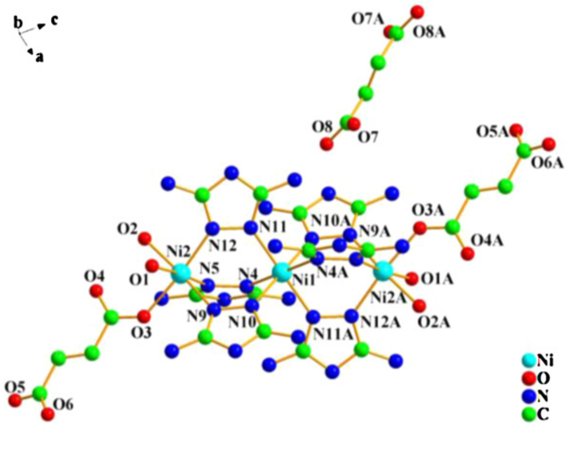

Fig. 1. Molecular structure of compound **1**, uncoordinated water molecules and H atoms are omitted for clarity.