Research Paper



Synthesis, crystal structure, and thermal properties of $Ni(NH_3)_4(AFT)_2$

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Abstract

Ni(NH₃)₄(AFT)₂ [NiC₆H₁₆N₁₈O₂, AFT = 4-amino-3-(5-tetrazolate)furazan] is synthesized and characterized by elemental analysis and Fourier-transform infrared spectroscopy for the first time. X-ray diffraction measurements are used to determine the crystal structure of compound I. The results demonstrate that compound I crystallized in the orthorhombic crystal system. The nickel(II) ion is six-coordinated by N atoms from two AFT-ligands and four NH₃ molecules. Its thermal properties are investigated by differential scanning calorimetry and thermogravimetry-derivative thermogravimetry methods, with the results demonstrating that the differential scanning calorimetry curve exhibits two endothermic and one exothermic processes. The endothermic processes are in the range of 130–510 °C with a peak temperature of 188 °C. The temperature from 230 to 400 °C is the exothermic process in which the peak temperature is 314.58 °C. In addition, Kissinger's and Ozawa-Doyle's methods are used for calculating the non-isothermal kinetics parameters. Moreover, the apparent activation energy (*E*), safety, and thermal stability parameters (T_{SADT} , T_{TIT} , T_b) for Ni(NH₃)₄(AFT)₂ are calculated. In addition, the calculated thermodynamic functions (ΔS^{\neq} , ΔH^{\neq} , and ΔG^{\neq}) for the exothermic decomposition process of Ni(NH₃)₄(AFT)₂ are 55.07 J mol⁻¹ K⁻¹, 196.18 kJ mol⁻¹, and 164.90 kJ mol⁻¹, respectively.

Keywords

crystal structure, 4-amino-3-(5-tetrazolate)furazan, nitrogen-rich heterocycles, synthesis, thermal behavior

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Figure 1. Molecular structure of complex 1.

Introduction

The preparation and design of high-density and low-sensitivity energetic materials, including pyrotechnics, propellants and explosives, are the focus of intense research interest in the chemical and materials industries. Energetic materials have found significant use in military and civilian applications during the past century.^{1–10} Although the early energetic materials demonstrate considerable performance, they often generate exhaust gases that are harmful to the environment. Further research is directed toward finding a balance between excellent performance and the environmental friendliness of energetic materials.¹¹

Efficient methods to promote the performance of energetic materials involve the utilization of nitrogen-rich heterocycles such as furazan, triazole, pyrazole, imidazole, tetrazole and their derivatives, which satisfy the pursuit of high-density, high-oxygen content and pollution-free generated gases.^{12–16} They all possess high positive heats of formation due to the presence of a large number of energetic bonds such as N-N, N=N, and N-C.17,18 What is more, nitrogenrich heterocycles such as furazan rings can ameliorate the performance of energetic materials, especially in terms of oxygen balance.¹⁹⁻²² Simple nitrogen-rich heterocycles materials are not a current focus in energetic material research, due to the requirements of higher energy and safer properties. Scientists have studied the combination of two or more nitrogen-rich heterocycles that can sharply promote energetic properties.^{23–27} The combination of tetrazole and furazan rings can eliminate the acidic proton and optimize the detonation properties.^{28,29} A furazan derivative, 4-amino-3-(5-tetrazolate)furazan (HAFT), first synthesized by Shreeve and colleagues,³⁰ is made up of amino, tetrazole, and furazan rings. This compound can be used to construct new multi-dimensional (one-, two-, three-dimensional (1D, 2D, 3D)) energetic metal-organic frameworks (MOFs) with several metal ions. Hence, a series of complexes of HAFT have been reported such as $[Cd(NH_2NH_2)(AFT)_2 \cdot 0.7H_2O]_n$, $[Cd(NH_2NHCOCONHNH_2)_{1.5}(AFT)_2 \cdot 5H_2O]_n$,³¹ $[Cd(H_2O)_2(AFT)_2]$,³² $[Cu(C_3H_6N_2H_4)_2(AFT)_2]$, $[Cu(NH_3)_4(AFT)_2]^{33}$ and $[Zn(NH_3)_4$ (AFT)₂],³⁴ which meet the needs of insensitive impact and thermal stability.

Herein, we have synthesized the new energetic complex $Ni(NH_3)_4(AFT)_2$. This complex will allow us to study the coordination chemistry of the metal ion. In addition, we have studied its crystal structure, thermal decomposition mechanism, and sensitivity properties.

Results and discussion

Structure description

Single-crystal X-ray diffraction (XRD) indicated that compound 1 belongs to the orthorhombic crystal system of the space group *Cmce*. It was observed that the structural unit of Ni(NH₃)₄(AFT)₂ (Figure 1) includes one nickel cation, four neutral ammonia molecules, and two AFT anions. The coordination environment of the Ni(NH₃)₄(AFT)₂ complex is similar to that of Cu(NH₃)₄(AFT)₂.³³ In contrast, this structure is different from that of Zn(NH₃)₄(AFT)₂.³⁴ Four neutral ammonia molecules and two AFT anions form a centrosymmetric structure with respect to the central Ni atom. A octahedral configuration is adopted by the Ni and N atoms, which are, respectively, from the central atom of the Ni(NH₂)₄(AFT)₂ complex, the AFT anion tetrazole ring [N(2), N(2A)] and the four ammonia molecules [N(8),N(8A), N(8B), N(8C)], which can form a six-coordinate environment. According to Table 1, the bond angles of the central Ni²⁺ and three contrapositioned N atoms are 180°

Table 1. Selected bond lengths (Å) and bond angles (°) for compound 1.

		· ·	
Bond	Distance (Å)	Angle	(°)
Ni(1)–N(2)	2.1088(15)	N(2)–Ni(1)–N(2A)	180.0
Ni(I)–N(2A)	2.1088(15)	N(8)-Ni(1)-N(8C)	180.0
Ni(1)–N(8)	2.1176(14)	N(8A)–Ni(1)–N(8B)	180.0
Ni(I)–N(8A)	2.1176(14)	N(2A)-Ni(1)-N(8)	89.07(5)
Ni(1)–N(8B)	2.1176(14)	N(2A)-Ni(1)-N(8A)	89.07(5)
Ni(1)-N(8C)	2.1176(14)	N(2A)-Ni(1)-N(8A)	89.07(5)
O(1)-N(5)	1.393(3)	N(2A)-Ni(1)-N(8C)	89.07(5)
O(I)-N(6)	1.376(3)	N(2)-Ni(1)-N(8B)	91.63(5)
N(I)–N(3)	1.338(2)	N(2)-Ni(1)-N(8A)	91.63(5)
N(I)-C(4)	1.337(3)	N(2)-Ni(1)-N(8C)	91.63(5)
N(2)–N(3)	1.318(2)	N(2)–Ni(1)–N(8)	91.63(5)
N(2)–N(4)	1.335(2)	N(8)-Ni(1)-N(8A)	88.36(6)
N(4)-C(4)	1.326(2)	N(8)–Ni(1)–N(8B)	88.36(6)
N(5)-C(5)	1.294(3)	N(8C)-Ni(1)-N(8A)	91.63(6)
N(6)-C(9)	1.285(3)	N(8C)-Ni(1)-N(8B)	91.63(6)

Table 2. Hydrogen bond lengths (Å) and bond angles (°) for compound I.

D–H…A	D–H (Å)	H…A (Å)	D–H…A (°)	
N(8)–H(8C)…N(5)#I	0.84(3)	2.47(3)	168(3)	
N(7)–H(7A)···O(1)#2	0.87(3)	2.25(2)	123(2)	
N(8)–H(8A)…N(1)#3	0.87(3)	2.61(2)	159(2)	
N(7)–H(7A)…N(4)#3	0.87(3)	2.28(3)	129(2)	

Symmetry codes: #1 I - x, -0.5 + y, 0.5 - z; #2 I - x, 0.5 + y, -0.5 + z; #3 I.5 - x, -y, -0.5 + z.



Figure 2. The 2D chain of complex I.

[<N(2)-Ni(1)-N(2A), <N(8)-Ni(1)-N(8C), <N(8A)-Ni(1)–N(8B)]. In addition, we surprisingly find that the bond angles of the N atoms and the Ni(II) ion are very close to 90° [<N(2A)-Ni(1)-N(8)=89.07(5)^{\circ}, <N(2A)-Ni(1)- $N(8A)=89.07(5)^{\circ}, < N(2A)-Ni(1)-N(8B)=89.07(5)^{\circ},$ $<N(2A)-Ni(1)-N(8C)=89.07(5)^{\circ}, <N(2)-Ni(1)-N(8)=$ 91.63(5)°, <N(2)-Ni(1)-N(8A)=91.63(5)°, <N(2)-Ni(1)-Ni(1)-N(8B)=88.37(10)°, <N(8)-Ni(1)-N(8A)=88.37(6)°, <N(8C)-Ni(1)-N(8A)=91.63(6)°, <N(8C)-Ni(1)-N(8B)= $88.37(6)^{\circ}$, $<N(8C)-Ni(1)-N(8B)=88.37(6)^{\circ}$]. Hence, these almost vertical bonds form a twisted octahedral geometry, where the equatorial plane is determined by four N atoms [N(8), N(8A), N(8B), N(8C)], and the axial plane is composed of two N atoms [N(2), N(2A)]. The data in Table 1 include the Ni bond lengths and the bond angles of the six N atoms surrounding Ni [Ni(1)-N(2) = 2.1088(15) Å,Ni(1)-N(2A) = 2.1088(15) Å, Ni(1)-N8(A/B/C) =2.1176(14) Å]. Thus, we can easily determine the axial plane, which includes two equivalent bonds, and is equally divided by the equatorial plane composed of four equidistant bonds.

Since there are many N and O atoms present in this compound, a significant number of hydrogen bonds are also present. As can be seen in Table 2, three intermolecular hydrogen bonds exist in the Ni complex. There is no intermolecular hydrogen bond between two Ni(NH₃)₄(AFT)₂ molecules, which are connected by van der Waals forces. As shown in Figure 2, the hydrogen bonds N(8)– H(8C)…N(5), N(7)–H(7A)…O(1), N(8)–H(8A)…N(1) and N(7)–H(7A)…N(4) and the molecule of Ni(NH₃)₄(AFT)₂



Figure 3. Packing structure of complex I.

form a two-dimensional structure. As illustrated in Figure 3, compound 1 is described as a 1D chain structure. Intermolecular hydrogen bonds between the AFT ligands and NH_3 molecules form the 2D supramolecular layer of complex 1 and can improve the thermal stability.

Thermal decomposition behavior

The thermal behavior of compound 1 was analyzed by differential scanning calorimetry (DSC) and thermogravimetry-derivative thermogravimetry (TG-DTG), with a linear heating rate of 10 °C min⁻¹ under a nitrogen atmosphere. The thermal behavior curves are shown in Figures 4 and 5. The DSC curve of compound 1 exhibits two exothermic and one endothermic processes. The exothermic process occurs from 230 to 400 °C, with a peak temperature of 314.58 °C. The endothermic process is in the range of 130-510 °C, with a peak temperature of 188 °C. As shown in the TG curve in Figure 6, the first mass loss stage occurs between 120 and 230 °C and reveals a weight loss of 17.11% during this period, which may be due to the loss of molecules of H₂O and the NH₃. The main mass loss of 48% of compound 1 occurs from 230 to 400 °C, where the DSC curve illustrates a sharply exothermic peak at 314.58 °C, and is probably due to decomposition of HAFT. The final mass loss stage of 29.03% can be ascribed to the decomposition of the residues and we observe a small exothermic peak at 462.37 °C as evidence of this in the DSC curves. It is very interesting that the major mass loss in compound 1, $\text{Cu}(\text{NH}_3)_4(\text{AFT})_2{}^{33}$ and $\text{Zn}(\text{NH}_3)_4(\text{AFT})_2{}^{34}$ all occur from the 200 to 400 °C. The main loss of mass from compound 1 occurs during the middle period of the TG process.



Figure 4. DSC curve of compound I at 10°C·min⁻¹.



Figure 5. TG-DTG curves of compound 1 at 10°C·min⁻¹

However, the main mass losses for $Cu(NH_3)_4(AFT)_2^{33}$ and $Zn(NH_3)_4(AFT)_2^{34}$ occur during the final period of the TG process. Although the peak temperature of compound **1** is lower than that of $Zn(NH_3)_4(AFT)_2$ (320.58 °C),³⁴ it is higher than those of $Cu(NH_3)_4(AFT)_2$ (310.92 °C), $Cu(C_3H_6N_2H_4)_2(AFT)_2$ (219.08 °C),³³ RDX (219 °C) and HMX (275 °C).³⁵ These data indicate that compound **1** possesses high thermal stability.

Non-isothermal kinetic analysis

The apparent activation energy (E_k/E_o) , pre-exponential factor (A_k) , and linear correlation coefficients (r_k/r_o) have been calculated by Kissinger's³⁶ and Ozawa-Doyle's³⁷ methods. These data are given in Table 3. The equations for Kissinger's and Ozawa-Doyle's methods are as follows

$$\ln \frac{\beta}{T_{\rm P}^2} = \ln \left[\frac{RA}{E_{\rm a}} \right] - \frac{E_{\rm a}}{R} \cdot \frac{1}{T_{\rm P}}$$
(1)

$$\log\beta + \frac{0.4567E}{RT_{\rm P}} = C \tag{2}$$

in which the linear heating rate is β , the peak temperature (K) is T_p , A is the pre-exponential constant (s⁻¹), the gas constant (8.314 J K⁻¹ mol⁻¹) is represented by *R*, and the apparent activation energy (kJ mol⁻¹) is referred to as *E*.

Based on the above data, the kinetic parameters, including the extrapolated onset temperature (T_e) and peak temperature (T_p) , have been calculated. The values of T_{e0} and T_{p0} (extrapolated temperature and peak temperature when the heating rates approach to 0) can be obtained through equation (3)

$$T_{(e \text{ or } p)i} = T_{(e^0 \text{ or } p^0)} + a\beta_i + b\beta_i^2 + c\beta_i^3 \qquad i = 1, 2, 3, 4$$
(3)

in which the coefficients are a, b and c.

The acquired E_a (the average of E_k and E_o) and A_k values can be used for expressing the Arrhenius equation of compound **1**, as follows

$$\ln k = 36.73 - 200.63 \times 10^3 / (RT)$$

Thermal stability, safety parameters, and thermodynamic functions

As is already known, the self-accelerating decomposition temperature (T_{SADT} or T_{e0}), thermal ignition temperature (T_{TIT} or T_{be0}) and critical temperature of thermal explosion (T_{b} or T_{bp0}) are important parameters, which can ensure safe storage and process operations for evaluating the thermal stability of energetic materials. The T_{SADT} , T_{TIT} and T_{b} values of compound 1 are calculated from equations (4) and (5), respectively (see Table 4), and are 265.69, 278.31 and 308.94 °C, respectively. We find that compound 1 shows preferable thermal stability in the exothermic decomposition stage

$$T_{\rm SADT} = T_{\rm e0} \tag{4}$$

$$T_{\rm be0(bp0)} = \left(E_O - \sqrt{E_O^2 - 4E_O R T_{\rm e0(p0)}}\right) / 2R$$
 (5)

The Ozawa method can be employed for obtaining the apparent activation energy (E_0) . In line with A and E_a , the thermodynamic parameters of the decomposition process of compound 1 were obtained. The entropy of activation $(\Delta S \neq)$, enthalpy of activation $(\Delta H \neq)$, and free energy of activation $(\Delta G \neq)$ of the main thermal decomposition reaction of complex 1 corresponding to $A = A_k$, $T = T_{p0}$ and $E_a = E_k$ can be computed from equations (6)–(8). The data are shown in Table 4

$$A = \left(k_B T / h\right) e^{\Delta S^* / R} \tag{6}$$

$$\Delta H^{\neq} = E_{a} - RT \tag{7}$$



Figure 6. TG-DSC curves of compound 1 at 10°C·min⁻¹.

$$\Delta G^{\neq} = \Delta H^{\neq} - T \Delta S^{\neq} \tag{8}$$

where $k_{\rm B}$ and *h* represent the Boltzmann constant $(1.381 \times 10^{-23} \,\mathrm{J K^{-1}})$ and the Planck constant $(6.626 \times 10^{-34} \,\mathrm{J s})$, respectively.

Compared with $Cd(pztza)_2$ and $Cd(pzpha)(CH_3OH)_2$,³⁸ the critical temperatures of which are 275.85 °C and 264.75 °C, compound 1 has a higher critical temperature.

Energy of combustion and enthalpy of formation

The energy of combustion $(\Delta_c H\theta)$, the enthalpy of formation $(\Delta_f H\theta)$, and the constant-volume energy of combustion $(\Delta_c U)$ of complex 1 were measured using an IKA C5000 oxygen bomb calorimeter. The value of $\Delta_c U$ is $-4933.61 \text{ kJ mol}^{-1}$. The bomb combustion reaction equations are displayed as follows

$$C_{6}H_{16}N_{18}O_{2}Ni(s)+19/2O_{2}(g)=NiO(s)+6CO_{2}(g) +8H_{2}O(1)+9N_{2}(g)$$
(9)

$$\Delta_c H_m^\theta = \Delta_c U_m + \Delta n R T \tag{10}$$

The standard molar enthalpy of combustion $(\Delta_c H\theta)$ can be verified by using equation (10). The parameter Δn is the change of the total molar amount of gases in the reaction process, and *R* and *T* are 8.314 J mol⁻¹ K⁻¹ and 298.15 K, respectively. The enthalpy of combustion of compound **1** is -4952.20 kJ mol⁻¹, which is lower than those of Cu(NH₃)₄(AFT)₂ (-4857.18 kJ mol⁻¹) and Zn(NH₃)₄(AFT)₂ (-4888.54 kJ mol⁻¹).

Hess' law and the combustion reactions were employed for obtaining the standard enthalpy of formation ($\Delta_{1}H\theta$) of compound **1**. The enthalpies of formation of CO₂ (g, -393.51 kJ mol⁻¹), H₂O (l, -285.83 kJ mol⁻¹), and NiO (s, -244.3 kJ mol⁻¹) are known, while the enthalpy of combustion of compound **1** is 60.20 kJ mol⁻¹.

Detonation property

The detonation parameters, including the detonation velocity (D), the detonation pressure (P), and the heat of detonation (Q), are significant for energetic performance evaluation in energetic materials. Currently, the largest exothermic principle proposed by Kamlet and Jacobs³⁹ is a valuable reference for research. Pang and colleagues⁴⁰ adopted a new empirical strategy to calculate these parameters that can be used as a basis to make predictions about metal-based energetic materials. It is easy to estimate the detonation reaction by using this strategy, which includes the arbitrary theory of Kamlet and Jacobs (K-J) and the hypothesis of the Becker–Kistiakowsky–Wilson (BKW) equation. The detonation reaction of compound **1** is described by equation (11). Furthermore, the K-J equations are given in equations (12)–(15)

$$C_6H_{16}N_{18}O_2Ni \rightarrow Ni + 2H_2O + 4NH_3 + 6C + 7N_2$$
 (11)

$$\mathbf{D} = 1.01 \Phi^{1/2} \left(1 + 1.30 \rho_0 \right) \tag{12}$$

$$P = 1.558 \Phi \rho_0^2$$
 (13)

$$\Phi = 31.68 N (MQ)^{1/2}$$
(14)

Table 3. Parameters determined from the DSC curves at different heating rates (β) for compound 1.

β (°C min ⁻¹)	T_{e} (°C)	$T_{\rm p}$ (°C)	<i>T</i> _{e0} (°C)	T_{p0} (°C)	E_{k} (kJ mol ⁻¹)	logA (s ⁻¹)	r _k	E_{o} (kJ mol ⁻¹)	r _o	Ē (kJ·mol⁻¹)
5.0	276.23	304.73	265.69	294.88	200.97	15.95	0.9858	200.29	0.9871	200.63
10.0	286.77	314.58								
15.0	294.69	317.36								
20.0	297.20	324.19								

Subscript k, data obtained by the Kissinger method; subscript o, data obtained by the Ozawa method.

Table 4. Values of T_{SADT} , T_{be0} , T_{bp0} , ΔS^{\neq} , ΔH^{\neq} , and ΔG^{\neq} for compound **I.**

Sample	T _{SADT} (°C)	<i>Т</i> _{ье0} (°С)	Т _{ьр0} (°С)	ΔS^{\neq} (J mol K ⁻¹)	∆H [≠] (kJ mol ⁻¹)	ΔG^{\neq} (kJ mol ⁻¹)
I	265.69	278.31	308.94	55.07	196.18	164.90

Sample	D (km s ⁻¹)	P (GPa)	Q (kJg ⁻¹)	
$Ni(NH_3)_4(AFT)_2$ (1)	5.54	13.15	1.894	
$Zn(NH_3)_3(AFT)_2$	5.41	12.80	2.673	
Cu(pn) ₂ (AFT) ₂	6.02	14.95	2.887	
Pb(HCONHNH ₂) ₂ (AFT) ₂	5.62	18.36	1.146	

Table 5. Detonation properties of compound I and some similar compound.





Scheme I. Preparation of HAFT.

Scheme 2. Synthesis of compound I.

$$Q = \frac{\Delta_f H_m^{\theta} (\text{denotation products}) - \Delta_f H_m^{\theta} (\text{explosive})}{\text{Formula weight of explosive}}$$
(15)

where D and P represent the detonation velocity (km s⁻¹) and the detonation pressure (GPa), respectively; the density of explosive (g cm⁻³) is ρ ; N can express the moles of detonation gases per gram of explosive; M is the average molecular weight of these gases; and the heat of detonation (kcal g⁻¹) is referred to as Q.

We can easily obtain many details from the above equations. The detonation velocity (D), the detonation pressure (P), and the heat of detonation (Q) were 5.54 km s^{-1} , 13.15 GPa, and $0.452 \text{ kcal g}^{-1}$ (1.894 kJ g^{-1}) for compound **1**. The detonation properties of some similar compounds are given in Table $5.^{41}$

From Table 5, it can be seen that. $Zn(NH_3)_3(AFT)_2^{34}$ has the lowest detonation velocity (D). The highest detonation pressure (P) of 18.36 GPa is exhibited by Pb(HCONHNH₂)₂ (AFT)₂. As for the heat of detonation (Q), Cu(pn)₂(AFT)₂ has the highest value of the compounds presented in Table 5.

Specific heat capacity

The continuous specific heat capacity of compound **1** was measured by using a Micro-DSC III instrument. Equation (16) accurately expresses the specific heat capacity equation of compound **1**. The specific heat capacity at 298.15 K is $1079.27 \text{ J g}^{-1} \text{ K}^{-1}$. Thus, the temperature is an essential factor that influences the specific heat capacity of compound **1**

$$C_{p} \left(\mathbf{J} \cdot \mathbf{g}^{-1} \mathbf{K}^{-1} \right) = 1.0102 + 1.2294 \times 10^{-2} T - 5.9527 \times 10^{-4} T^{2}$$
$$+ 1.7228 \times 10^{-5} T^{3} - 2.2246 \times 10^{-7} T^{4}$$
$$+ 1.0309 \times 10^{-9} T^{5}$$

Impact sensitivity

The impact sensitivity (IS) is considered to be a significant property of energetic materials from the view point of personal safety. Energetic materials are required to be insensitive, which can reduce the risk of unnecessary accidents. The data on the IS were obtained using a drop hammer IS device with a 2.5 kg hammer weight at a height of 1.2 m. The experiment revealed that compound 1 had a lower IS (15.9 J), being less sensitive than $Zn(NH_3)_4(AFT)_2^{34}$ (15.0 J), $Cu(NH_3)_4(AFT)_2^{33}$ (12.0 J), and HMX^{42} (7.4 J). The advantage of this IS makes compound 1 an interesting candidate as a new, safe energetic material.

Conclusion

In conclusion, $Ni(NH_3)_4(AFT)_2$ has been synthesized for the first time and structurally characterized. Ni(NH₃)₄(AFT)₂ crystallized in the orthorhombic space group Cmce. Moreover, the DSC and TG-DTG curves show that $Ni(NH_2)_4(AFT)_2$ possesses one endothermic decomposition peak and two exothermic decomposition peaks, the former is sharp and the latter is smooth, and the thermal decomposition processes can be divided into three stages. The endothermic process is in the range of 130-510 °C with a peak temperature of 188 °C. The exothermic process occurs from 230 to 400°C, with a peak temperature of 314.58 °C. The self-accelerating decomposition temperature (T_{SADT}), thermal ignition temperature (T_{TIT}), and critical temperature of thermal explosion $(T_{\rm b})$ for $Ni(NH_3)_4(AFT)_2$ are 265.69, 278.31, and 308.94 °C, respectively, which indicate good thermal safety. The non-isothermal kinetic analysis data indicate the Arrhenius equation can be expressed as $\ln k = 36.73 - 200.63 \times 10^3 / (RT)$. At the same time, complex 1 shows higher density $(1.700 \,\mathrm{g \, cm^{-3}})$ and a relatively low IS (15.9J), being much lower than RDX and HMX. Therefore, Ni(NH₃)₄(AFT)₂ should be investigated further as a competitive energetic material.

Experimental

(16)

Most energetic materials are flammable and explosive substances. In some experiments, many harmful substances

Compound I	
Chemical formula	NiC ₆ H ₁₆ N ₁₈ O ₂
Formula weight (g mol ⁻¹)	431.08
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	Стсе
Size (mm)	0.21×0.16×0.18
Volume (ų)	1684.3(5)
Ζ	4
$D_{\text{calc}} (\text{g cm}^{-3})$	1.700
F(000)	888
θ range (°)	2.070–26.109
Index ranges	$-7 \le h \le 8, -24 \le k \le 20, -15 \le l \le 14$
Reflections collected	4411
Reflections unique	917
Refinement method	Full-matrix least-squares on F^2
R(int)	0.0236
a (Å)	6.9055(11)
b (Å)	19.676(3)
c (Å)	12.3964(19)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
Goodness-of-fit on F^2	1.048
$R_{ } [l > 2r(l)]$	0.0219
$wR_{2} [I > 2r(I)]$	0.0611
R ₁ (all data)	0.0246
wR ₂ (all data)	0.0628
CCDC	1903740

Table 6.	Crystal	data an	d structure	refinement	details	of
compound	1 I.					

CCDC: Cambridge Crystallographic Data Centre.

are produced, such as strong acids and bases. Therefore, extreme care should be taken when conducting these experiments. Appropriate protective equipment must be used.

Materials and methods

All chemicals were commercially available reagents of analytical grade and used directly. A VarioEL III elemental analyzer (Elementar Co., Germany) was used to record the elemental analysis. An EQUINX55 infrared spectrometer was used to acquire the Fourier-transform infrared spectroscopy (FTIR) spectrum as a KBr pellet in the range of 4000–500 cm⁻¹. DSC was performed using a DSC-Q2000 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of 50 mLmin⁻¹, with heating rates (β) of 5, 10, 15, and 20 °C min⁻¹ from 70 to 470 °C. The TG-DTG experiment was implemented with an SDT-Q600 apparatus (TA, USA) under the conditions of a flow of nitrogen gas with a flow rate of 100 mLmin⁻¹ and a heating rate of 10.0 °C min⁻¹. A ZBL-B IS instrument (Nachen Co., China) was used for determining the IS.

Preparation of HAFT

A three-step literature procedure was used to synthesized HAFT in Scheme 1.⁴³

Synthesis of $[Ni(NH_3)_4](AFT)_2(I)$

HAFT (0.3828 g, 2.5 mmol) was dissolved in deionized water (5 mL) and charged into a glass reactor with a water bath. The reaction solution was stirred with a mechanical agitator and heated at ambient temperature. Ni(NO₃)₂ (0.1914 g, 1.25 mmol) dissolved in 5 mL of deionized water was added to HAFT solution during 15 min. Then, aqueous ammonia solution (1mL) was added to the above-mentioned reacting mixture under constant stirring. The solution was stirred for an additional 60 min. Finally, filter residue was filtered out. The mother liquor was sealed and left at room temperature (Scheme 2). Appropriate crystals for X-ray measurements were obtained after 2 months. m.p.: 155-155.8 °C. Anal. calcd. for NiC₆H₁₆N₁₈O₂: C, 16.72; H, 3.74; N, 58.50; found: C, 16.74; H, 3.72; N, 58.46. IR (KBr): 3491 (w, -NH₂), 3365 (m, -NH), 1639 (m, -C=O), 1594 (m, N=N), 1200 (m, -C-N), 1171 (s, -C-N), 987 (m, -NH₃), 865 (w, -NH₂), 667 (s, -NH₃).

Crystal structure determination and refinement

The single-crystal X-ray determination was carried out with a Bruker SMART APEX CCD X-ray diffractometer using graphite-monochromated Mo-*Ka* radiation (λ = 0.71073 nm) and an φ - ω scan mode at 296(2) K. The structures were resolved by direct methods (SHELXTL-97) and optimized by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms.^{44,45} The hydrogen atoms were determined with theoretical models. CheckCIF was used for checking the finalized Crystallographic Information File (CIF) file. The refinement parameters and crystallographic data for Ni(NH₃)₄(AFT)₂ are collected in Table 6.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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