Synthesis, structure analysis and thermal behavior of two new complexes: Cu(NH$_3$)$_4$(AFT)$_2$ and Cu(C$_3$H$_6$N$_2$H$_4$)$_2$(AFT)$_2$

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A B S T R A C T

Two new energetic complexes base on nitrogen-rich compound 4-amino-3-(5-tetrazolate)-furazan: Cu(NH$_3$)$_4$(AFT)$_2$ (**1**) and Cu(C$_3$H$_6$N$_2$H$_4$)$_2$(AFT)$_2$ (**2**) were synthesized by reaction of Cu(NO$_3$)$_2$·3H$_2$O with ammonia and diaminopropane. For complexes **1** and **2**, they were fully characterized by EA and FT-IR. The crystal structure of complex **1** was determined by single-crystal X-ray diffraction. X-ray single-crystal diffraction analysis revealed that the complex **1** crystallized in orthorhombic crystal system. The thermal decomposition behaviors of the two complexes were studied with DSC and TG/DTG methods. The non-isothermal kinetics parameters were calculated by the Kissinger's method and Ozawa-Doyle's method for the main exothermic decomposition processes of the title compounds. Moreover, the entropy of activation ($\Delta S^{\neq}$), the enthalpy of activation ($\Delta H^{\neq}$) and the free energy of activation ($\Delta G^{\neq}$) were calculated. The specific heat capacity (C_p) and mechanical sensitivity were also investigated.

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1. Introduction

Designing new generation energetic molecules with high performance and low sensitivity has always garnered significant attention [1–4]. Recently, the pursuit of high-performance energetic materials, 1,2,5-oxadiazole (furazan), gradually continue being the research hot-spot due to its high density and high oxygen content [5–7]. However, due to the absence of an acidic proton, the furazan ring fails to bond with metal ions and thus furazan-based energetic metal compounds have received relatively less consideration. Meanwhile, due to the positive heat of formation and thermal stability, nitrogen-rich heterocyclic rings such as triazole, tetrazole, imidazole, tetrazine and their derivatives [8–18] as ligands to construct energetic coordination compounds have also received a great deal of interest and thereby offering intriguing structural backbones for the design and construction of new high-energy density materials (HEDMs). In this direction, combination of the furazan and tetrazole rings has proven to be a good strategy for the synthesis of new high-nitrogen compounds, which not only removes the acidic proton, but also improves properties [19–21].

A furazan derivative, 4-amino-3-(5-tetrazolate)-furazan (HAFT) is composed of amino, tetrazole and furazan rings. Undoubtedly, it is propitious to constructing energetic frameworks with outstanding physicochemical properties by HAFT. Nitrogen-rich energetic salts based on HAFT have been reported, which are insensitive to impact and are thermally stable. Such as G (AFT), AG (AFT), DAG (AFT), TAG (AFT) [19,22]. So we want to prepare some HAFT complexes and explore their structure-property relationship. Due to the fact that Copper (II) possesses varied coordination numbers and can form complexes with various structures, we prepared two copper-HAFT complexes to explore.

Now we first synthesize two new exciting copper complexes of HAFT, which have been confirmed via single-crystal X-ray structure analysis for complex **1** and other tests. This work will enrich the research on the coordination chemistry of HAFT.
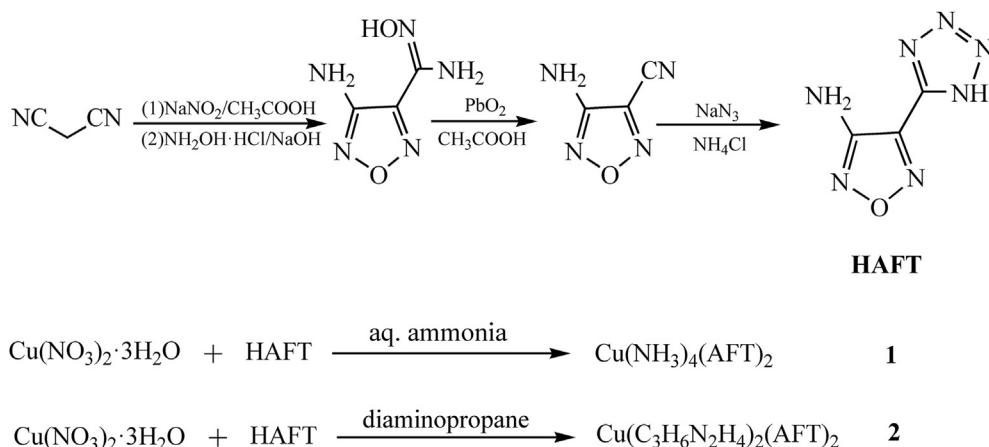
2. Experimental

2.1. Materials and analyses

All chemicals were analytical-grade commercial products. HAFT was prepared according to Ref. [23], the synthesis route of as Scheme 1.

Elemental analyses (C, H and N) were performed on a VarioEL III

Scheme 1. Synthesis of **HAFT**, **1** and **2**.

elemental analyzer (Elementar Co., Germany). Fourier Transform Infrared (FT-IR) were determined with KBr pellet for solids by using a EQUINX55 spectrometer in the range of 4000-500 cm^{-1}. Differential scanning calorimeter (DSC) tests were determined using a DSC-Q2000 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of 50 mL min^{-1}, the heating rates (β) were 5, 10, 15 and 20 °C·min^{-1} from ambient temperature to 370 °C. TG-DTG experiment were carried out with a SDT-Q600 apparatus (TA, USA) under the nitrogen gas condition with a flow rate of 100 mL min^{-1} at a heating rate of 10.0 °C·min^{-1}. The specific heat capacity (C_p) experiments were determined with a Micro-DSC III apparatus (SETARAM, France) with the operating temperature range of 283—333 K. The impact sensitivity experiments were determined by using a ZBL-B impact sensitivity instrument (Nachen Co., China).

2.2. Synthesis of Cu(NH$_3$)$_4$(AFT)$_2$ (1)

1 was synthesized as follows: HAFT (2.5 mmol) was dissolved in distilled water (5 mL), and charged into a glass reactor with a water bath. It was kept under mechanical stirring and heated to the temperature of 60—65 °C. Cu(NO$_3$)$_2$·3H$_2$O (0.25 mol/L, 5 mL) was added to the HAFT solution during 15 min with continuous stirring. Then, aqueous ammonia solution (1 mL) was added and the mixture was kept at 60—65 °C for 60 min. Afterwards the solution was cooled to room temperature. The resulting mixture was filtered and allowed to evaporate in an undisturbed condition at ambient temperature. In the end, single crystal suitable for X-ray measurement was obtained by evaporation of the mother liquor at room temperature for one week. Yield: 60.3%. CuC$_6$N$_{18}$H$_{16}$O$_2$: calcd. C 16.53; H 3.70; N 57.84%. Found: C 16.50; H 3.74; N 57.83%. IR (KBr): 3453, 3326, 3253, 3178, 1630, 1565, 1428, 1363, 1261, 1232, 1156, 988, 912, 862, 699, cm^{-1}.

2.3. Synthesis of Cu(C$_3$H$_6$N$_2$H$_4$)$_2$(AFT)$_2$ (2)

2 was synthesized as follows: HAFT (2.5 mmol) was dissolved in distilled water (5 mL), and charged into a glass reactor with a water bath. It was kept under mechanical stirring and heated to the temperature of 60—65 °C. Cu(NO$_3$)$_2$·3H$_2$O (0.25 mol/L, 5 mL) was added to the HAFT solution during 15 min with continuous stirring. Then, diaminopropane solution (1 mL) was added and the mixture was kept at 60—65 °C for 60 min. Afterwards the solution was cooled to room temperature. The resulting mixture was filtered and allowed to evaporate in an undisturbed condition at ambient temperature. In the end, small single crystal was obtained by evaporation of the mother liquor at room temperature for one day.

Yield: 50.1%. CuC$_{12}$N$_{18}$H$_{24}$O$_2$: calcd. C 22.52; H 5.04; N 52.53%. Found: C 22.50; H 5.06; N 52.60%. IR (KBr): 3666, 3485, 3367, 3307, 3253, 2970, 2875, 1622, 1593, 1463, 1357, 1278, 1062, 981, 910, 684, 617, cm^{-1}.

2.4. Crystal structure determinations

Single-crystal X-ray diffraction data were collected on a Bruker SMART APEX-II CCD X-ray diffractometer equipped with a graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by the direct methods (SHELXTL-97) and refined by the full-matrix-block least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms [24,25]. The finalized CIF file was checked with checkCIF. Crystallographic data and refinement parameters of **1** are gathered in Table 1 (CCDC No.: 1843781).

3. Results and discussion

3.1. Crystal structure

Single-crystal X-ray diffraction studies indicate that complex **1** crystallizes in the orthorhombic crystal system with the space

Table 1
Crystal data and structure refinement details of **1**.

complex	**1**
Empirical formula	CuC$_6$N$_{18}$H$_{16}$O$_2$
Formula weight (g·mol^{-1})	435.91
Temperature (K)	296 (2)
Crystal system	orthorhombic
Space group	P nma
a (Å)	19.204 (5)
b (Å)	7.127 (16)
c (Å)	12.422 (3)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	1700.1 (7)
Z	4
D$_{calc}$/(g·cm^{-3})	1.703
F (000)	892
θ range/°	2.68—20.51
Goodness-of-fit on F^2	1.033
R$_1$ [I > 2r(I)]	0.0410
wR$_2$ [I > 2r(I)]	0.0961
R$_1$ (all data)	0.0652
wR$_2$ (all data)	0.1053
CCDC	1843781