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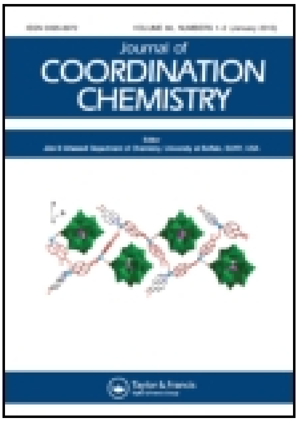

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# Two new copper-FOX-7 complexes: synthesis, crystal structure, and thermal behavior

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Two new copper complexes, $[Cu(phen)_2FOX\text{-}7](phen)NO_3{\cdot}4H_2O$ and $[Cu(phen)_2FOX\text{-}7]Cl{\cdot}3H_2O$ (phen = 1,10-phenanthroline monohydrate; FOX-7 = 1,1-diamino-2,2-dinitroethylene) were synthesized and structurally characterized. Single crystal X-ray diffraction shows that Cu(II) in the two complexes has similar five-coordinate structure, including four nitrogens from two phen and one nitrogen from FOX-7 anion. Thermal decomposition behaviors of the two complexes were studied with differential scanning calorimetry and thermogravimetry/differential thermogravimetry methods. The apparent activation energies and pre-exponential constants of the main exothermic decomposition reaction for the two complexes are 208.1 and 183.1 $kJ\,mol^{-1}$, $10^{22.99}$ and $10^{19.19}$ $s^{-1}$, respectively. The self-accelerating decomposition temperature and critical temperature of thermal explosion for the two complexes are 152.64 and 162.17 °C, 161.50 and 173.29 °C, respectively.

*Keywords*: 1,1-Diamino-2,2-dinitroethylene (FOX-7); 1,10-Phenanthroline monohydrate (phen); Coordination complex; Crystal structure; Thermal behavior

## 1. Introduction

Cu(II) phen complexes attract attention for their properties used in catalytic reaction, electrochemistry, molecular biology, and other fields [1–7]. Many energetic Cu(II) complexes are used as detonating explosive or combustion catalysts of solid propellant [8–15]. 1,1-Diamino-2,2-dinitroethylene (FOX-7) is a novel high-energy material with high thermal stability and low sensitivity. When first synthesized in 1998 [16], FOX-7 received much attention for synthesis [16–19], reaction mechanism [20], molecule structure [21], theoretical calculations [22–26], thermal behavior [27, 28], explosive performance [29, 30], and the application of FOX-7 [31]. According to the molecular structure features, FOX-7 is a special "push–pull" nitro-enamine compound [32], which possesses a highly polarized carbon–carbon double bond with positive and negative charges stabilized by two amino groups and two nitro groups, respectively, and presents certain acidic properties. So, FOX-7 can react with strong alkalis to prepare some energetic salts [33–36], such as potassium salt, rubidium salt, cesium salt, and guanidine salt. Through replacement

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reaction, other salts and metal complexes of FOX-7 can be synthesized using potassium or guanidine salt of FOX-7 as starting material. Garg *et al*. reported the structures and properties of Ag(amine)(FOX-7) [amine: ammonia, methylamine, and propylamine] and Cu(amine)$_2$(FOX-7)$_2$ [amine: ammonia, methylamine, propylamine and dimethylamine, ethylenediamine, and 1,3-propane diamine] [37, 38]. Reactivity of FOX-7 is still a popular field. In our studies on FOX-7, two new complexes, [Cu(phen)$_2$FOX-7](phen)NO$_3$·4H$_2$O (**1**) and [Cu(phen)$_2$FOX-7]Cl·3H$_2$O (**2**), were synthesized and expected to be used as combustion catalyst in solid propellant. In this article, we report their crystal structures and thermal decomposition behaviors, and explore copper coordination in different surrounding environments.

## 2. Experimental

### 2.1. *Materials and physical measurements*

All chemicals used in synthesis were analytical-grade commercial products. FOX-7 came from Xi'an Modern Chemistry Research Institute (purity > 99%). K(FOX-7)·H$_2$O was prepared according to the literature [36].

Elemental analyses were performed on a VarioEL Ш elemental analyzer (Elementar Co., Germany). IR spectra were determined on an EQUINX55 with KBr pellets. UV-vis spectra were measured on a SHIMADZU UV-3600 spectrophotometer from 200 to 800 nm. Differential scanning calorimetry (DSC) and thermogravimetry/differential thermogravimetry (TG/DTG) curves under flowing nitrogen (purity, 99.99%) were obtained by using a SDT-Q600 thermal analyzer (TA Co., USA). The heating rates were 5, 10, 15, and 20 °C min$^{-1}$ from ambient to 550.0 °C.

### 2.2. *Synthesis*

**2.2.1. [Cu(phen)$_2$FOX-7](phen)NO$_3$·4H$_2$O.** 1,10-Phenanthroline monohydrate (0.297 g, 1.5 mmol) was added to a solution of Cu(NO$_3$)$_2$·3H$_2$O (0.121 g, 0.5 mmol in 3 mL of water) and placed into an oil bath at 85 °C until phenanthroline dissolved. Powdered K(FOX-7)·H$_2$O (0.094 g, 0.5 mmol) was then added into the solution and stirred for 30 min in the oil bath. Blue–green precipitate of [Cu(phen)$_2$FOX-7](phen)NO$_3$·4H$_2$O (**1**) was formed, filtered, and dried under vacuum, yielding 0.274 g (61.9%). Anal. Calcd (%) for $C_{38}H_{35}CuN_{11}O_{11}$: C, 51.55; H, 3.98; N, 17.40. Found (%): C, 51.08; H, 3.22; N, 18.21. IR (KBr, *v*/cm$^{-1}$): 3386, 3213, 3058, 2921, 2852, 1644, 1597, 1509, 1456, 1425, 1252, 1137, 843, 776, 718, 636, 472.

**2.2.2. [Cu(phen)$_2$FOX-7]Cl·3H$_2$O.** 1,10-Phenanthroline monohydrate (0.297 g, 1.5 mmol) was added to a solution of CuCl$_2$ (0.135 g, 1 mmol in 3 mL of water) and placed into a water bath at 70∼80 °C until the phenanthroline dissolved. FOX-7 (0.074 g, 0.5 mmol) was added, and then solution of KOH (0.06 g in 3 mL of water) was added to the solution and stirred for 1 h in the oil bath. Green [Cu(phen)$_2$FOX-7]Cl·3H$_2$O (**2**) was formed, filtered, and dried under vacuum, yielding 0.199 g (60.3%). Anal. Calcd (%) for $C_{26}H_{25}ClCuN_8O_7$: C, 47.28; H, 3.81; N, 16.96. Found (%): C, 47.09; H, 3.64; N, 16.38. IR (KBr, *v*/cm$^{-1}$): 3534, 3407, 3291, 3220, 2921, 2852, 2510, 1998, 1625, 1513, 1464, 1424, 1382, 1340, 1241, 1129, 851, 780, 721, 633, 474.

### 2.3. *Determination of the single crystal structure*

Single crystals for the two complexes were obtained from their reaction filtrates through evaporation of solvent. The two crystals are green. X-ray diffraction data were collected on a Bruker SMART APEX CCD X-ray diffractometer using graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.071073$ nm). The structures were solved by direct methods (SHELXTL-97) and refined by full-matrix-block least-squares on $F^2$ with anisotropic thermal parameters for all non-hydrogen atoms [39]. Hydrogens were added according to theoretical models. Crystal data and refinement results are summarized in table 1 and selected bond lengths and angles in table 2.

## 3. Results and discussion

### 3.1. *Crystal structure*

Crystals of the two complexes are both triclinic with space group of *P−1*; but, the two complexes also have special structure features. Complex **1** has an uncoordinated phen, whereas **2** does not. Complex **1** contains a monovalent coordination cation $[\mathrm{Cu(phen)_2\text{-}FOX\text{-}7}]^+$, a close neighboring nitrate, an uncoordinated phen, and four lattice waters (figure 1). Cu(II) is coordinated by N1, N2, N3, and N4 from two phen and N5 from an

Table 1. Crystal data and structure refinement details.

| Compound | **1** | **2** |
|---|---|---|
| Chemical formula | $C_{38}H_{35}CuN_{11}O_{11}$ | $C_{26}H_{25}ClCuN_8O_7$ |
| Formula weight/(g mol$^{-1}$) | 885.31 | 660.53 |
| Temperature/K | 296(2) | 296(2) |
| Crystal system | Triclinic | Triclinic |
| Space group | *P−1* | *P−1* |
| *a* (Å) | 9.123(2) | 9.2160(13) |
| *b* (Å) | 10.752(3) | 10.8289(15) |
| *c* (Å) | 20.285(5) | 14.840(2) |
| *α* (°) | 80.293(5) | 88.822(2) |
| *β* (°) | 88.984(4) | 78.173(2) |
| *γ* (°) | 74.439(4) | 74.342(2) |
| Volume/Å$^3$ | 1888.6(8) | 1394.8(3) |
| *Z* | 2 | 2 |
| $D_{calc}$/g cm$^{-3}$ | 1.543 | 1.573 |
| Absorption coefficient/mm$^{-1}$ | 0.657 | 0.911 |
| *F*(000) | 898 | 678 |
| *θ* range (°) | 2.63–25.10 | 1.40–28.61 |
| Index ranges | $-11 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 13$, $-25 \leqslant l \leqslant 20$ | $-12 \leqslant h \leqslant 11$, $-14 \leqslant k \leqslant 12$, $-14 \leqslant l \leqslant 19$ |
| Reflections collected/unique | 10,126/7312 [R(int) = 0.0518] | 8546/6258 [R(int) = 0.0237] |
| Goodness-of-fit on $F^2$ | 0.996 | 0.999 |
| Final *R* indices [$I > 2\sigma(I)$] | $R_1 = 0.0770$, $wR_2 = 0.1762$ | $R_1 = 0.0692$, $wR_2 = 0.1489$ |
| *R* indices (all data) | $R_1 = 0.0787$, $wR_2 = 0.2365$ | $R_1 = 0.0470$, $wR_2 = 0.1215$ |
| Largest diff. peak and hole/(e·Å$^{-3}$) | 0.756 and −0.716 | 0.614 and −0.530 |

Table 2. Selected bond lengths (Å) and angles (°) of **1** and **2**.

| Complex **1** | | Complex **2** | |
|---|---|---|---|
| Cu(1)–N(5) | 1.959(5) | Cu(1)–N(5) | 1.968(3) |
| Cu(1)–N(3) | 2.103(5) | Cu(1)–N(3) | 2.093(3) |
| Cu(1)–N(2) | 1.998(5) | Cu(1)–N(2) | 1.992(3) |
| Cu(1)–N(1) | 2.131(5) | Cu(1)–N(1) | 2.157(3) |
| Cu(1)–N(4) | 2.007(5) | Cu(1)–N(4) | 1.999(3) |
| C(26)–C(27) | 1.510(9) | C(25)–C(26) | 1.479(4) |
| N(5)–C(26) | 1.284(8) | N(5)–C(25) | 1.296(4) |
| N(6)–C(26) | 1.322(8) | N(6)–C(25) | 1.326(4) |
| N(7)–C(27) | 1.376(8) | N(7)–C(26) | 1.369(4) |
| N(8)–C(27) | 1.367(8) | N(8)–C(26) | 1.376(4) |
| N(5)–Cu(1)–N(2) | 95.1(2) | N(5)–Cu(1)–N(2) | 95.65(11) |
| N(5)–Cu(1)–N(3) | 133.1(2) | N(5)–Cu(1)–N(3) | 138.40(10) |
| N(5)–Cu(1)–N(1) | 118.6(2) | N(5)–Cu(1)–N(1) | 118.39(10) |
| N(3)–Cu(1)–N(1) | 108.13(19) | N(3)–Cu(1)–N(1) | 103.11(10) |
| N(5)–Cu(1)–N(4) | 90.5(2) | N(5)–Cu(1)–N(4) | 90.84(11) |
| N(2)–Cu(1)–N(3) | 95.6(2) | N(2)–Cu(1)–N(3) | 94.07(10) |
| N(2)–Cu(1)–N(1) | 80.3(2) | N(2)–Cu(1)–N(1) | 80.05(10) |
| N(2)–Cu(1)–N(4) | 174.3(2) | N(2)–Cu(1)–N(4) | 173.46(10) |
| N(4)–Cu(1)–N(3) | 80.0(2) | N(4)–Cu(1)–N(3) | 80.49(10) |
| N(4)–Cu(1)–N(1) | 97.5(2) | N(4)–Cu(1)–N(1) | 97.56(11) |

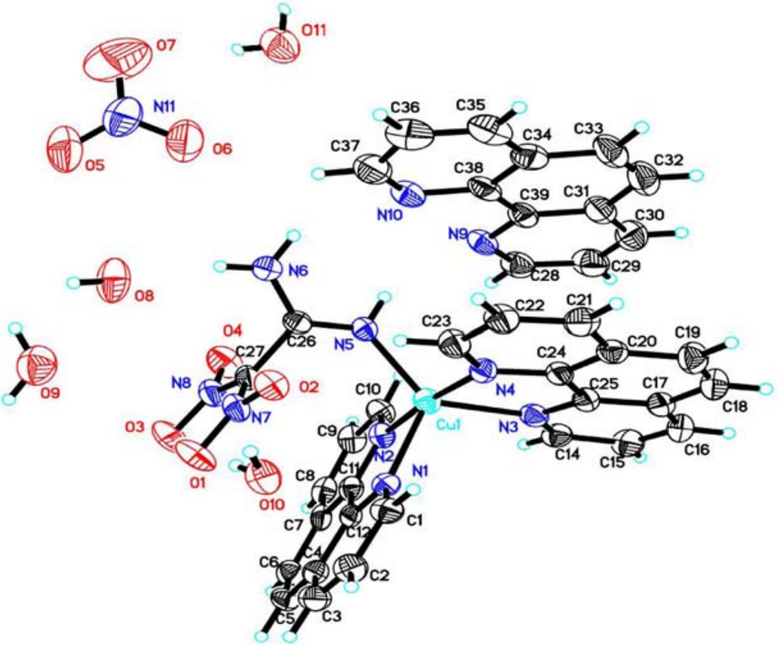

Figure 1. Molecular structure of **1**.

amino of FOX-7 anion. N5 has lost hydrogen in the process. The geometry of the crystal about each five-coordinate copper is distorted square–pyramidal with N2, N3, N4, and N5, making the plane and N1 as the vertex. As the crystal structure shows in figure 2, a nitrate has coulomb and hydrogen bond interactions with the complex. There are two hydrogen

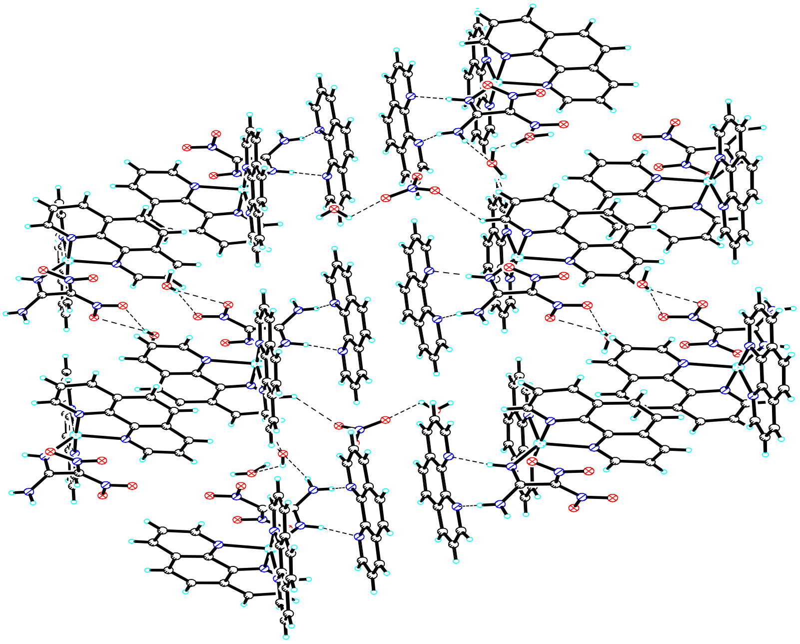

Figure 2. View of the 2D layer for **1**.

bond interactions between nitrate and lattice water. The uncoordinated phen is nearly parallel with one coordinated phen. Each uncoordinated phen interconnects through two hydrogen bonds [N5–H5A···N9 and N6–H6A···N10] with two amino groups of a FOX-7 anion.

Complex **2** contains a monovalent coordination cation $[Cu(phen)_2FOX\text{-}7]^+$, a close neighboring chloride, and three lattice waters (figure 3). Cu(II) is coordinated by N1, N2, N3, and N4 from two phen and N5 from an amino group of FOX-7 anion, as for **1**. The coordination atoms and Cu(II) form a distorted square–pyramidal structure with N2, N3, N4, and N5, forming the plane of the square pyramid. The bond angles of N5–Cu1–N2, N2–Cu1–N3, N4–Cu1–N3, and N5–Cu1–N4 are 95.65(11)°, 94.07(10)°, 80.49(10)°, and 90.84(11)°, respectively, and the summation of the bond angles around copper is close to 360°. N2, N3, N4, and N5 are almost coplanar with Cu1, but N1 is in the axial position. Although Cu(II) forms square-pyramidal configuration in the two complexes, **2** is more regular than **1**. The Cu1–N1, Cu1–N2, Cu1–N3, and Cu1–N4 bond lengths are 2.157(3), 1.992(3), 2.093(3), and 1.999(3) Å, respectively. The average Cu–N bond length (2.0606 Å) is slightly longer than Cu1–N5 (1.9683 Å), and so the coordination capability of phen is weaker than that of FOX-7 anion. Coordinations of four nitrogens from phen are different and their bond lengths are 2.157(3), 1.992(3), 2.093(3), and 1.999(3) Å, respectively. The Cu1–N1 bond length is slightly longer than that of others, leading to N1 as the vertex of the geometry. From figure 4, we can see that there are two weak hydrogen bond interactions between lattice waters [O6–H11B···O5, O7–H7B···O6] and three hydrogen bond interactions between FOX-7 anion and lattice waters (N6–H6B···O7#2, O5–H5B···O1 and O5–H5B···O3). Chloride combines to the complex via three hydrogen bond interactions [N5–H5···Cl#1, N6–H6A···Cl#1 and O7–H7A···Cl] and Coulomb interaction.

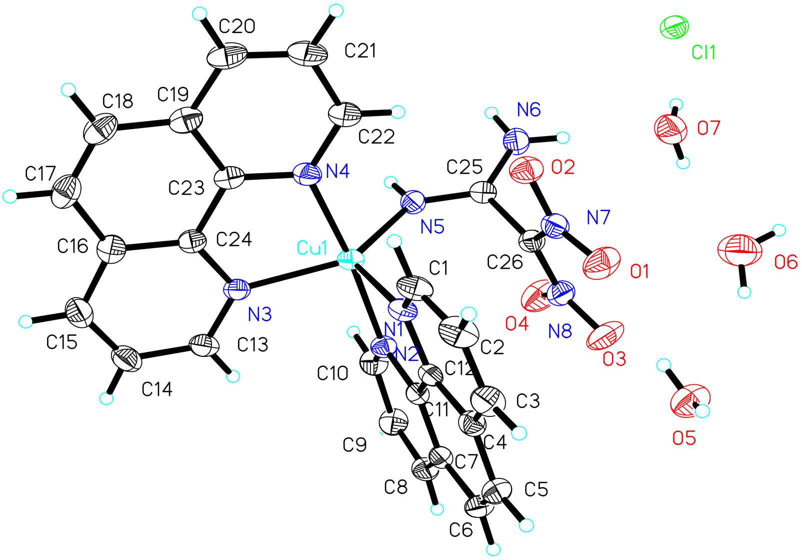

Figure 3. Molecular structure of **2**.

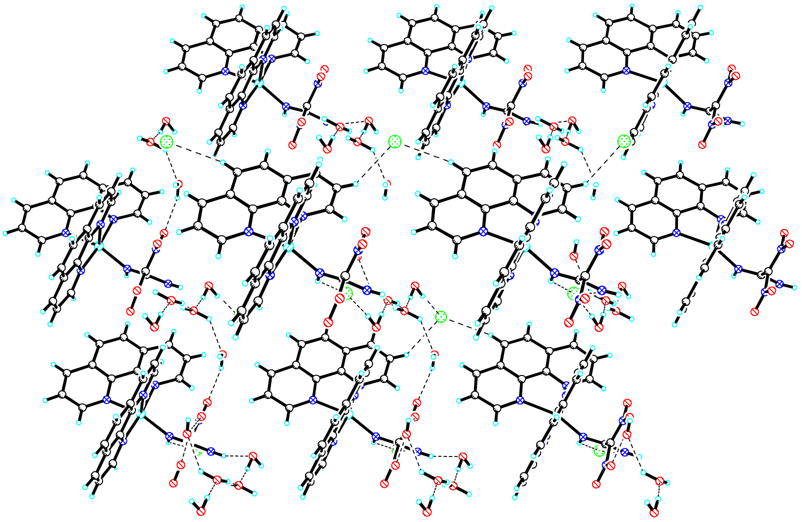

Figure 4. View the 2D layer for **2**.

Those hydrogen bond interactions contribute significantly to the stability of complex. Hydrogen bond distances and angles are listed in table 3.

Comparing with other energetic Cu(II) complexes [8–15], we can see that the coordination format of central Cu(II) can form four-coordinated structure [8], five-coordinated structure [9–11], and six-coordinated structure [12–15], according to different ligands and different synthetic conditions. The two new copper-FOX-7 complexes are both five-coordinate. Crystal waters all are free and do not take part in coordination, and so they are easy to lose in heating.

Table 3. Hydrogen bonds for **1** and **2** (Å and °).

| D–H···A | *d*(D–H) | *d*(H···A) | *d*(D···A) | ∠(DHA) |
|---|---|---|---|---|
| Complex **1** | | | | |
| N5–H5A···N9 | 0.860 | 2.195 | 2.956 | 169.76 |
| N6–H6A···N10 | 0.860 | 2.440 | 3.127 | 137.38 |
| O8–H18C···O9 | 0.900 | 2.122 | 2.793 | 131.75 |
| O9–H14B···O10#1 | 0.900 | 2.269 | 2.746 | 112.79 |
| O10–H10A···O2 | 0.858 | 2.342 | 2.930 | 126.01 |
| O6–H6B···O3 | 0.858 | 2.562 | 3.385 | 160.97 |
| Complex **2** | | | | |
| N5–H5···Cl#2 | 0.860 | 2.682 | 3.399 | 141.76 |
| N6–H6A···Cl#2 | 0.860 | 2.421 | 2.896 | 160.65 |
| N6–H6B···O7#3 | 0.900 | 2.485 | 3.166 | 132.79 |
| O6–H11B···O5#3 | 0.900 | 2.583 | 3.051 | 113.12 |
| O7–H7A···Cl | 0.850 | 2.317 | 3.154 | 168.49 |
| O7–H7B···O6 | 0.810 | 2.024 | 2.746 | 148.25 |
| O5–H5B···O1 | 0.801 | 2.152 | 3.168 | 167.88 |
| O5–H5B···O3 | 0.801 | 2.506 | 3.028 | 124.08 |
| O5–H5C···O2#4 | 0.820 | 2.148 | 2.943 | 163.61 |

Note: Symmetry transformations used to generate the equivalent atoms: #1: $x-1$, $y$, $z$; #2: $-x+1$, $-y+1$, $-z$; #3: $-x+1$, $-y+1$, $-z+1$; #4: $-x$, $-y+1$, $-z+1$.

In the two complexes, the configuration of FOX-7 anion changes from originally one plane to two approximately orthogonal planes (all non-hydrogens) [40]; the intersection of the two approximate orthogonal planes is the C(1)–C(2) bond. The configuration change can be found in other salts of FOX-7 because of all kinds of forces. Comparing bond lengths and angles with that of FOX-7, many change greatly. The symmetrical and approximately equal bond lengths and angles in FOX-7 are no longer consistent through different interactions. Theoretical C–C double bond (1.51 and 1.48 Å) in FOX-7 anion is much closer to C–C single bond (1.53 Å) than in FOX-7 (1.45 Å) [21]. Two equal C–N ($NH_2$) bonds present big deviation [1.284 and 1.322 Å for **1** and 1.296 and 1.326 Å for **2**]. C–NH bond in FOX-7 anion is a typical C–N double bond in the two complexes. FOX-7 has changed into its tautomer.

### 3.2. *IR spectra and UV-vis spectra*

In IR spectra of **1,** adsorptions at 854 and 740 cm$^{-1}$ in 1,10-phen attributed to $\delta_{\text{C–C}}$ and $\delta_{\text{C–H}}$, shift to 842 and 718 cm$^{-1}$, respectively, confirming coordination. Adsorptions at 3404, 3330, 3298, and 3323 cm$^{-1}$ corresponding to N–H shift to 3212, 3057, 2920, and 2852 cm$^{-1}$ due to amino group of FOX-7 anion. Bands in the 400–480 cm$^{-1}$ region are an indicative of Cu–N coordination [41]. The adsorption of –OH from $H_2O$ is at 3386 cm$^{-1}$. The adsorption at 1597 cm$^{-1}$ is $\nu_{\text{C=N}}$ in phen, from uncoordinated phen. The data are in agreement with the crystallographic results. In IR spectra of **2,** adsorptions at 854 and 740 cm$^{-1}$ also shift to 851 and 720 cm$^{-1}$ attributed to $\delta_{\text{C–C}}$ and $\delta_{\text{C–H}}$ from phen, respectively. Adsorption of N–H from FOX-7 anion is also red-shifted. Bands at 400–480 cm$^{-1}$ indicate Cu–N coordination [41]. The –OH from $H_2O$ is at 3533 cm$^{-1}$.

UV-vis spectra of **1** display adsorption at 712 nm, attributed to $d\rightarrow d$ transition of $Cu^{2+}$ [41]. The phen exhibits adsorption at 290 nm, assigned to $\pi\rightarrow\pi^*$ transition. The adsorption band of FOX-7 anion is at 216 nm, assigned to $\pi\rightarrow\pi^*$ transition. The adsorption at

260 cm$^{-1}$ can be attributed to uncoordinated 1,10-phen. UV-vis spectra of **2** display the adsorption at 670 nm, assigned to $d \rightarrow d$ transition of $Cu^{2+}$. The two peaks at 270 and 224 nm can be assigned to $\pi \rightarrow \pi^*$ transition of phen and FOX-7, respectively.

Having the same cupric ion, phen and FOX-7 anion, the two complexes present many similar spectral features.

### 3.3. *Thermal analysis*

From the DSC and TG–DTG curves (figures 5 and Supplementary Material), **1** undergoes three major stages of weight loss. Four crystal waters are removed between 50 and 125 °C, leading to a total weight loss of 7.3% (theoretical value 8.1%) and giving an obvious endothermic peak at 92.80 °C in the DSC curve at heating rate of 10 °C min$^{-1}$. The second weight loss occurs at 150–225 °C with mass loss of 12.0%, which is an intense exothermic decomposition. The peak temperature and decomposition enthalpy of the process at heating rate of 10 °C min$^{-1}$ are 170.8 °C and $-299.2$ kJ mol$^{-1}$, respectively. The third weight loss occurs at 225–400 °C with 35.9%, giving a weak exothermic process from 299.25 °C to 340.10 °C in the DSC curve. The final residue at 600 °C is about 45.3%. Complex **2** also undergoes three major decomposition stages (Supplementary Material). The first stage is dehydration of three crystal waters at 50–120 °C with a weight loss of 7.8% (theoretical value 7.2%) and the endothermic peak temperature is 102.26 °C in the DSC curve at 10 °C min$^{-1}$. The second stage is an intense exothermic decomposition, which occurs at 130–200 °C with a weight loss of 14.8%. The peak temperature and decomposition enthalpy of the process at heating rate of 10 °C min$^{-1}$ are 185.56 °C and $-355.9$ kJ mol$^{-1}$, respectively. The third stage occurs at 240–500 °C with a weight loss of 51.1%, giving several weak exothermic processes in the DSC curve. The final residue at 600 °C is 24.5%. The two complexes have similar decomposition behaviors with thermal stability of **2** higher than that of **1**.

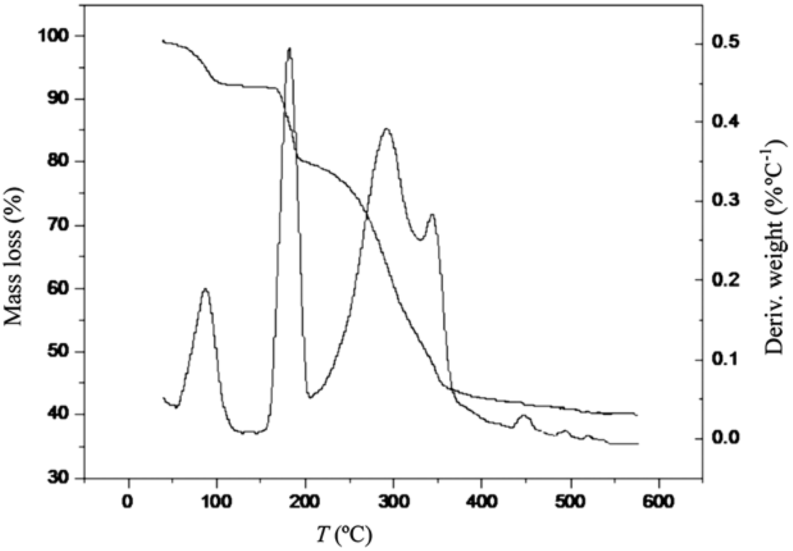

Figure 5. TG–DTG curves of **1** at 10 °C min$^{-1}$.

In order to obtain kinetic parameters (the apparent activation energy ($E$) and pre-exponential constant ($A$)) of the intense exothermic decomposition stages for the two complexes, multiple heating methods (Kissinger method [42] and Ozawa method [43]) were employed. The determined values of the extrapolated onset temperature ($T_e$), peak temperature ($T_p$), and decomposition enthalpy ($\Delta H_d$) of the exothermic decomposition processes at the different heating rates are listed in table 4. The values of $T_{e0}$ corresponding to $\beta \to 0$ obtained by equation (1) are also listed in table 4 [44].

$$T_{ei} = T_{e0} + n\beta_i + m\beta_i, \ i = 1\text{–}4 \tag{1}$$

where $n$ and $m$ are coefficients.

The calculated values of $E$ and $A$ are listed in table 5. The apparent activation energies obtained by Kissinger method are consistent with those by the Ozawa method for the two complexes. The linear correlation coefficients ($r$) are very close to 1. So, the results are credible.

The self-accelerating decomposition temperature ($T_{\mathrm{SADT}}$) and critical temperature of thermal explosion ($T_b$) are two important parameters required to insure safe storage and process operations for energetic materials and then to evaluate the thermal stability. $T_{\mathrm{SADT}}$ and $T_b$ can be obtained by equations (2) and (3) [44, 45], respectively.

$$T_{\mathrm{SADT}} = T_{e0} \tag{2}$$

$$T_b = \frac{E_O - \sqrt{E_O^2 - 4E_O \mathrm{RT}_{e0}}}{2R} \tag{3}$$

with $E_O$ as the apparent activation energy obtained by the Ozawa method.

Table 4. Basic data for the main exothermic decomposition of **1** and **2**.

| | $\beta$/(K min$^{-1}$) | $T_e$/°C | $T_p$/°C | $\Delta H$/(J g$^{-1}$) | $T_{e0}$/°C |
|---|---|---|---|---|---|
| Complex **1** | 5 | 156.94 | 166.03 | −232.13 | 152.64 |
| | 10 | 160.58 | 170.80 | | |
| | 15 | 164.23 | 173.96 | | |
| | 20 | 167.00 | 176.58 | | |
| Complex **2** | 5 | 170.30 | 179.47 | −508.93 | 162.17 |
| | 10 | 175.96 | 185.56 | | |
| | 15 | 179.85 | 189.41 | | |
| | 20 | 182.54 | 192.13 | | |

Table 5. Kinetic parameters obtained by the data in Table 4.

| | $E_k$/(kJ mol$^{-1}$) | log ($A_k$/s$^{-1}$) | $r_k$ | $E_O$/(kJ mol$^{-1}$) | $r_O$ | $\bar{E}$/(kJ mol$^{-1}$) |
|---|---|---|---|---|---|---|
| Complex **1** | 209.7 | 22.99 | 0.9985 | 206.4 | 0.9996 | 208.1 |
| Complex **2** | 184.0 | 19.19 | 0.9999 | 182.2 | 0.9999 | 183.1 |

Notes: Subscript k and O, data obtained by Kissinger method and Ozawa method.
$\bar{E}$ is the mean value of the apparent activation energy by two methods.

$T_{\mathrm{SADT}}$ and $T_{\mathrm{b}}$ for **1** are 152.64 and 161.50 °C, while $T_{\mathrm{SADT}}$ and $T_{\mathrm{b}}$ for **2** are 162.17 and 173.29 °C, respectively. From the results, **2** has higher thermal stability than **1**. However, the difference for the two complexes is small because of similar composition and coordination structure.

## 4. Conclusion

Two new copper complexes were synthesized based on FOX-7 and phen as ligands. The crystals are both triclinic with space groups of *P−1*. Coppers are both five-coordinate, one from FOX-7$^{-}$ and the other four from two phen. The two complexes have similar IR and UV-vis. The decomposition enthalpies, apparent activation energies, and pre-exponential constants of the main exothermic decomposition process for the two complexes are $-299.2$ and $-355.9\,\mathrm{kJ\,mol^{-1}}$, 208.1 and $183.1\,\mathrm{kJ\,mol^{-1}}$, and $10^{22.99}$ and $10^{19.19}$ $\mathrm{s^{-1}}$, respectively. The self-accelerating decomposition temperature and critical temperature of thermal explosion for the two complexes are 152.64 and 162.17 °C, 161.50 and 173.29 °C, respectively. Complex **2** has higher thermal stability than **1**.

## Supplementary material

CCDC-876376 (**1**) and CCDC-887782 (**2**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge, CB2, 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk.

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## References

[1] O.O.E. Onawnmi, O.O.P. Fabya, O.A. Odunola, T.K. Prasad, M.V. Rajasekharan. *Polyhedron*, **30**, 725 (2001).

[2] C.K. Tseng, C.R. Lee, C.C. Han, S.G. Shyu. *Chem. Eur. J.*, **17**, 2716 (2011).

[3] C.W. Yaw, W.T. Tan, W.S. Tan, C.H. Ng, W.B. Yap, N.H. Rahman, Mohamed Zidan. *Int. J. Electrochem. Sci.*, **7**, 4692 (2012).

[4] A. Kellett, M. O'Connor, M. McCann, M. McNamara, P. Lynch, G. Rosair, V. McKee, B. Creaven, M. Walsh, S. McClean, A. Foltyn, D. O'Shea, O. Howe, M. Devereux. *Dalton Trans.*, **40**, 1024 (2011).

[5] W. Li, C.H. Li, Y.Q. Yang, Y.F. Kuang. *J. Struct. Chem.*, **27**, 210 (2008).

[6] W.T. Wang, S.P. Chen, G. Fan, G. Xie, B.J. Jiao, S.L. Gao. *J. Coord. Chem.*, **62**, 1879 (2009).

[7] B.J. Jiao, S.P. Chen, F.Q. Zhao, R.Z. Hu, S.L. Gao. *J. Hazard. Mater.*, **142**, 550 (2007).

[8] G. Fan, Y.L. Zhang, J.J. Sun, M.Y. Zheng. *J. Coord. Chem.*, **64**, 3711 (2011).

[9] Q. Yang, S.P. Chen, G. Xie, S.L. Gao. *J. Coord. Chem.*, **65**, 2584 (2012).

[10] J.J. Liu, Z.L. Liu, J. Cheng. *J. Solid State Chem.*, **197**, 198 (2013).

[11] M. Friedrich, J.C.G. Ruiz, T.M. Klapötke, P. Mayer, B. Weber, J.J. Weigand. *Inorg. Chem.*, **44**, 8044 (2005).

[12] Q. Yang, S.P. Chen, G. Xie, S.L. Gao. *J. Hazard. Mater.*, **197**, 199 (2011).

[13] J. Stierstorfer, K.R. Tarantik, T.M. Klapötke. *Chem. Eur. J.*, **15**, 5775 (2009).

[14] T.M. Klapötke, J. Stierstorfer, B. Weber. *Inorg. Chim. Acta*, **362**, 2311 (2009).

[15] G.H. Tao, B. Twamley, J.M. Shreeve. *Inorg. Chem.*, **48**, 9918 (2009).

[16] N.V. Latypov, J. Bergman, A. Langlet, U. Wellmar, U. Bemm. *Tetrahedron*, **54**, 11525 (1998).

[17] H.Q. Cai, Y.J. Shu, H. Huang, B.B. Cheng, J.S. Li. *J. Org. Chem.*, **69**, 4369 (2004).

[18] G. Hervé, G. Jacob, N. Latypov. *Tetrahedron*, **61**, 6743 (2005).

[19] W.A. Trzciński, S. Cudzilo, Z. Chylek, L. Szymańczyk. *J. Hazard. Mater.*, **157**, 605 (2006).

[20] M. Anniyappan, M.B. Talawar, G.M. Gore, S. Venugopalan, B.R. Gandhe. *J. Hazard. Mater.*, **137**, 812 (2006).

[21] U. Bemm, H. Ötmark. *Acta Crystallogr., Sect. C*, **54**, 1997 (1998).

[22] A. Gindulyte, L. Massa, L. Huang, J. Karle. *J. Phys. Chem. A*, **103**, 11045 (1999).

[23] D.C. Sorescu, J.A. Boatz, D.L. Thompson. *J. Phys. Chem. B*, **107**, 8953 (2003).

[24] D.C. Sorescu, J.A. Boatz, D.L. Thompson. *J. Phys. Chem. B*, **109**, 1451 (2005).

[25] F.J. Zerilli, M.M. Kuklja. *J. Phys. Chem. A*, **111**, 1721 (2007).

[26] J.J. Zhao, H. Liu. *Comput. Mater. Sci.*, **42**, 698 (2008).

[27] H.X. Gao, F.Q. Zhao, R.Z. Hu, Q. Pan, B.Z. Wang, X.W. Yang, Y. Gao, S.L. Gao, Q.Z. Shi. *Chin. J. Chem.*, **24**, 177 (2006).

[28] X.Z. Fan, J.Z. Li, Z.R. Liu. *J. Phys. Chem. A*, **111**, 13291 (2007).

[29] G. Majano, S. Mintova, T. Bein, T.M. Klapötke. *J. Phys. Chem. C*, **111**, 6694 (2007).

[30] A.V. Kimmel, P.V. Sushko, A.L. Shluger, M.M. Kuklja. *J. Phys. Chem. A*, **112**, 4496 (2008).

[31] B. Buszewski, M. Michel, S. Cudzilo, Z. Chylek. *J. Hazard. Mater.*, **164**, 1051 (2009).

[32] S. Rajappa. *Tetrahedron*, **37**, 1453 (1981).

[33] K.Z. Xu, C.R. Chang, J.R. Song, F.Q. Zhao, H.X. Ma, X.Q. Lű, R.Z. Hu. *Chin. J. Chem.*, **26**, 495 (2008).

[34] K.Z. Xu, J.R. Song, F.Q. Zhao, H.X. Ma, H.X. Gao, C.R. Chang, Y.H. Ren, R.Z. Hu. *J. Hazard. Mater.*, **158**, 333 (2008).

[35] K.Z. Xu, F.Q. Zhao, J.R. Song, X.L. Ren, H.X. Gao, S.Y. Xu, R.Z. Hu. *Bull. Korean Chem. Soc.*, **30**, 225 (2009).

[36] K.Z. Xu, X.G. Zuo, J.R. Song, F. Wang, J. Huang, C.R. Chang. *Chem. J. Chin. Univer.*, **31**, 638 (2010).

[37] S. Garg, H.X. Gao, Y.H. Joo, D.A. Parrish, Y. Huang, J.M. Shreeve. *J. Am. Chem. Soc.*, **132**, 8888 (2010).

[38] S. Garg, H.X. Gao, D.A. Parrish, J.M. Shreeve. *Inorg. Chem.*, **50**, 390 (2011).

[39] G.M. Sheldrick. *SHELXL-97, Program for X-ray Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany (1997).

[40] K.Z. Xu, J.R. Song, X. Yang, C.R. Chang, X.K. Yang, H.X. Ma, J. Huang, F.Q. Zhao. *J. Mol. Struct.*, **891**, 340 (2008).

[41] A.M.A. Bennett, G.A. Foulds, D.A. Thornton. *Spectrochim. Acta*, **45**, 219 (1989).

[42] H.E. Kissinger. *Anal. Chem.*, **29**, 1702 (1957).

[43] T. Ozawa. *Bull. Chem. Soc. Jpn.*, **38**, 1881 (1965).

[44] R.Z. Hu, S.L. Gao, F.Q. Zhao, Q.Z. Shi, T.L. Zhang, J.J. Zhang. *Thermal Analysis Kinetics*, 2nd Edn, Science Press, Beijing (2008), in Chinese.

[45] T.L. Zhang, R.Z. Hu, Y. Xie, F.P. Li. *Thermochim. Acta*, **244**, 171 (1994).