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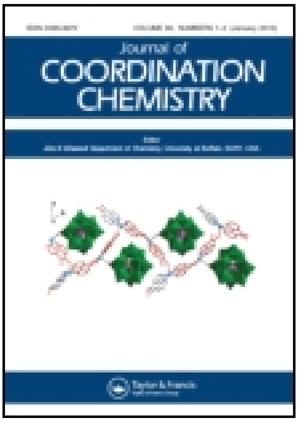

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Synthesis, structure, and thermal behavior of a 2-D polymeric Ca(II) compound with tetrazole-1-acetic acid

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Synthesis, structure, and thermal behavior of a 2-D polymeric Ca(II) compound with tetrazole-1-acetic acid

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A 2-D polymeric Ca(II) compound, $[Ca(tza)_2(H_2O)_2]_n$, was synthesized by the reaction of tetrazole-1-acetic acid with calcium carbonate. The product was characterized by X-ray single-crystal diffraction, elemental analysis, and IR spectroscopy. The calcium center is six-coordinate in a slightly distorted octahedral configuration by four carboxylic oxygens from four different tza^- ligands and two waters. The 2-D supramolecular laminar structure in *b*-axis × *c*-axis plane was constructed via four bridging tza^- ions connecting one Ca(II) with four adjacent Ca(II) ions. Differential scanning calorimetry and thermogravimetric–differential thermogravimetric analysis were applied to assess the thermal decomposition behavior. The kinetic parameters were obtained by non-isothermal reaction kinetics, and the Arrhenius equation can be expressed as $\ln k = 21.96 – 262.2 \times 10^3/RT$. The values of critical temperature of thermal explosion, $\Delta S^{\neq}$, $\Delta H^{\neq}$, and $\Delta G^{\neq}$ were obtained as 574 K, $-67.62\,J\,mol^{-1}\,K^{-1}$, $257.52\,kJ\,mol^{-1}$, and $295.59\,kJ\,mol^{-1}$, respectively.

Keywords: Calcium complex; Tetrazole-1-acetic acid; Crystal structure; Thermal behavior

1. Introduction

Tetrazole derivatives have attracted attention due to their fascinating structures and interesting properties. In the recent years, there has been considerable interest in tetrazole derivatives as metal organic frameworks [1–3], monolithic nano-porous metal foams [4] and energetic materials [5–9]. Tetrazole-based energetic materials show the best compromise between high performance, low sensitivity, and moderate thermal stability. Hence, they gain more attention as potential energetic materials [10–18]. Tetrazole-1-acetic acid (Htza) is a carboxyl-substituted tetrazole derivative.

Htza as a multifunctional ligand with both carboxylate oxygens and tetrazolyl ring nitrogens has been used to design and synthesize functional coordination compounds with

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*Corresponding author. Email: ztlbit@bit.edu.cn potential applications and intriguing geometries [19–22]. He *et al.* that reported the crystal structures and magnetic properties of nanoscale $Cu_{12}Ln_6$ clusters were constructed by dinuclear and multidentate tza and other inorganic ligands [23]. Coordination polymers of lanthanide(III) with tza were investigated by Yu and his co-workers [24], and magnetic measurements show weak antiferromagnetic coupling between the metal centers in Pr(III) and Nd(III) complexes. Xu *et al.* reported the crystal structures and properties of Cd(II), Mn(II), Co(II), Zn(II), Cu(II) and Ag(I) coordination polymers with tza [22, 23, 25]. Heavy metal complexes of tza, $[Pb(tza)_2]_n$ [26] and $[Bi(tza)_3]_n$ [27], were investigated as energetic burning rate catalysts of solid propellents by Li and Wang *et al.* Most of these studies are focused on lanthanide and transition metals; complexes with main group elements are rare. The K(I) salt of tza was reported as a potential flame sensitivity energetic compound [28].

Interests have focused on alkaline earth coordination polymers due to their topologies and potential applications in gas storage, separation, catalysis, magnetism, and luminescence as well as energetic materials [29–37]. In 2009, Klapötke *et al.* [30] reported the structures and properties of environment-friendly energetic materials and alkaline earth metal salts of 5-nitro-2H-tetrazole. In 2012, Yang *et al.* [29] reported the coordination architectures and luminescent properties of 5-(pyrimidyl)tetrazolate with group 2 metal ions. Coordinated to various ligands, Ca(II) can construct many different architectures [34–37]. Kong *et al.* [34] reported the seven-coordinate calcium(II) complex with 1-D structures and Starosta *et al.* [36] reported the 3-D polymeric molecular pattern in the structure of a Ca(II) complex with pyrazine-2,3,5,6-tetracarboxylate and water ligands.

Herein, we synthesized an alkaline earth complex of tza, $[Ca(tza)_2(H_2O)_2]_n$, and investigated the crystal structure and thermal behavior.

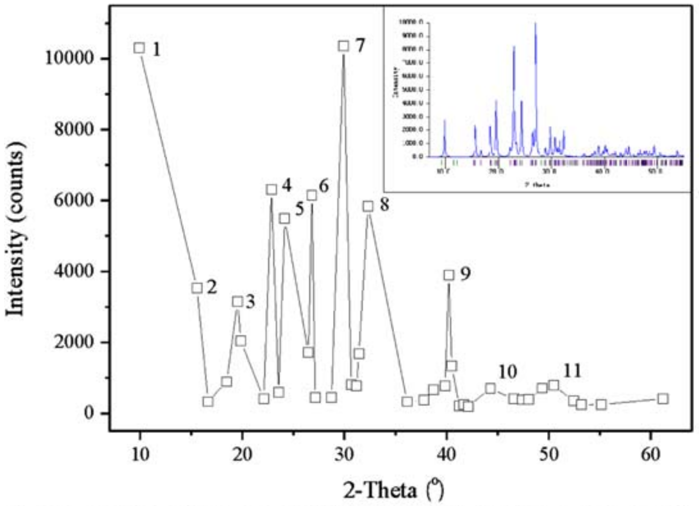
2. Experimental

2.1. *General method*

Calcium carbonate and Htza are analytically pure commercial products. Elemental analyses (carbon, hydrogen, and nitrogen) were performed on an Elementar Vario MICROCUBE (Germany) full-automatic trace element analyzer. FT-IR spectra were recorded with a Bruker Equinox 55 infrared spectrometer (KBr pellets, 4000–400 cm^{-1} with a resolution of 4 cm^{-1}, Germany). Powder XRD analysis was determined by the D8 ADVANCE X-ray diffractometer (Bruker, Germany). Thermal behavior was investigated by differential scanning calorimeter (DSC) (CDR-4, Shanghai Precision & Scientific Instrument Co., Ltd) and thermogravimetric analysis (TGA) (Pyris-1, Perkin-Elmer, USA). The sample (about 0.5 mg) was placed in aluminum pans in static air for DSC at various heating rates (5, 10, 15, 20 °C min^{-1}) from 50 to 600 °C. TG measurements were performed at a heating rate of 10 °C min^{-1} in platinum sample pans using dry nitrogen with a flow rate of 20 mL min^{-1}.

2.2. *Synthesis of $[Ca(tza)_2(H_2O)_2]_n$*

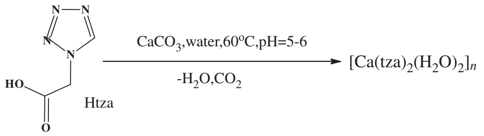
Htza (0.64 g, 5 mmol) was dissolved in 10 mL deionized water at 60 °C. As $CaCO_3$ (0.25 g, 2.5 mmol) was slowly added, a large amount of carbon dioxide was generated. The pH of the resulting solution was adjusted with Htza to 5–6. The mixtures were kept reacting for one hour at 60 °C with stirring, then, the solvent was removed under vacuum.



(1: (1 0 0), d=8.911; 2: (1 1 0), d=5.686; 3: (1 1 1), d=3.890; 4: (2 1 -1),d=3.681; 5: (0 2 0), d=3.324; 6: (2 1 1), d=2.984; 7: (3 0 0), d=2.846; 8: (3 1 0), d=2.770; 9: (4 0 0), d=2.240; 10: (2 3 1), d=2.043; 11: (0 1 5), d=1.805)

Figure 1. Powder XRD patterns of $[Ca(tza)_2(H_2O)_2]_n$.

When cooled to room temperature, the solid product precipitated was washed with ethanol and dried in a water bath oven at 50 °C to yield the product as white powder. Yield 85.4%, based on $CaCO_3$. The mother liquor was allowed to slowly concentrate by evaporation at room temperature yielding colorless crystals (suitable for X-ray analysis) after 7 days. Anal. Calcd. (%) for $[Ca(tza)_2(H_2O)_2]_n$: C, 21.82; H, 3.05; N, 33.93. Found: C, 21.90; H, 3.14; N, 33.65. IR (KBr pellet) data (ν cm^{-1}): 3446, 3134, 1631, 1448, 1427, 1402, 1319, 1180, 1107, 983, 802, 694, 579. The powder XRD pattern of the product was obtained and shown in figure 1. The determined data correspond well to the calculated powder pattern by the single-crystal data, which was present in the top-right corner of figure 1.



2.3. *X-ray crystallography*

A colorless single crystal with dimensions of 0.37 mm × 0.33 mm × 0.17 mm was selected for X-ray diffraction analysis. X-ray diffraction data collection was performed on a Rigaku AFC-10/Saturn 724^+ CCD diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) at 93(2) K using the multiscan technique. The structure of $Ca(tza)_2 \cdot (H_2O)_2$ was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares procedures on F^2 with SHELXL-97 [38–40]. Anisotropic thermal parameters were applied

Table 1. Crystallographic data and structure determination details for $[Ca(tza)_2(H_2O)_2]_n$.

Empirical formula	$Ca(C_3H_3N_4O_2)_2 \cdot (H_2O)_2$
Formula weight ($g\,mol^{-1}$)	330.28
Temperature (K)	93(2)
Crystal dim. (mm)	0.17 × 0.33 × 0.37
Crystal system	Monoclinic
Space group	$P2(1)/c$
a (Å)	9.352(3)
b (Å)	7.293(2)
c (Å)	9.922(3)
β (°)	106.198(4)
V (Å^3)	649.9(4)
Z	2
ρ ($g\,cm^{-3}$)	1.688
μ (mm^{-1})	0.528
$F(0\,0\,0)$	340
θ ranges (°)	3.52–27.48
Limiting indices	$-10 \leqslant h \leqslant 12$ $-7 \leqslant k \leqslant 9$ $-12 \leqslant l \leqslant 12$
Reflections collected	4168
Independent reflections (R_{int})	1461(0.0339)
Data/restraints/parameters	1461/0/113
Goodness-of-fit on F^2	0.884
Final R_1, wR_2 $[I > 2\sigma(I)]^a$	0.0410, 0.1161
R_1, wR_2 indices (all data)^a	0.0521, 0.1291
Largest difference in peak and hole ($e\,Å^{-3}$)	0.359 and −0.384

$^a w = 1/[\sigma^2(F_o)^2 + (0.1000P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$

to all non-hydrogen atoms. Hydrogens connected to carbon were generated geometrically and hydrogens of water were located from difference maps and refined with isotropic temperature factors. Crystallographic data and experimental details for structure analysis are summarized in table 1.

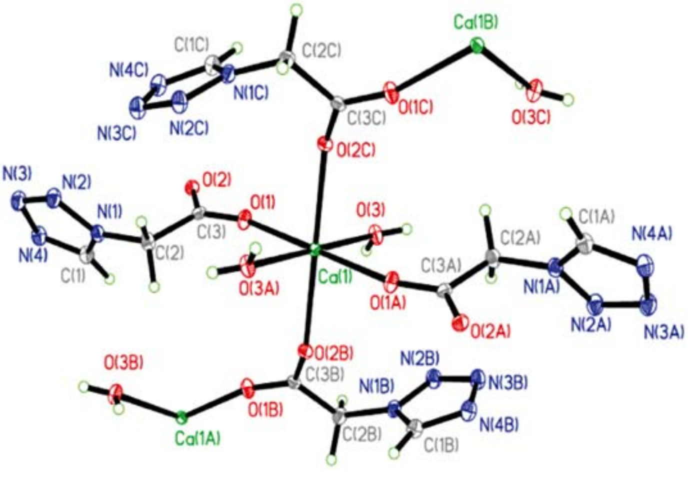


Figure 2. Molecular structure and coordination environment of calcium in $[Ca(tza)_2(H_2O)_2]_n$.

Table 2. Selected bond lengths (Å) and angles (°) for $[Ca(tza)_2(H_2O)_2]_n$.

Bond lengths (Å)					
Ca(1)–O(1)	2.279(2)	Ca(1)–O(2)#3	2.282(2)	N(1)–C(1)	1.332(3)
Ca(1)–O(3)	2.403(2)	O(1)–C(3)	1.245(2)	N(1)–N(2)	1.347(3)
Ca(1)–O(2)#1	2.282(2)	O(2)–C(3)	1.253(3)	N(2)–N(3)	1.297(3)
Ca(1)–O(1)#2	2.279(2)	C(2)–C(3)	1.526(3)	N(3)–N(4)	1.363(3)
Ca(1)–O(3)#2	2.403(2)	N(1)–C (2)	1.455(3)	N(4)–C(1)	1.314(3)
Angles (°)					
O(1)–Ca(1)–O(3)	86.87(6)	O(1)#3–Ca(1)–O(2)#1	89.53(5)	N(3)–N(2)–N(1)	106.19(17)
O(1)–Ca(1)–O(2)#1	90.47(5)	O(2)#1–Ca(1)–O(3)#3	92.95(6)	N(2)–N(3)–N(4)	110.93(18)
O(1)–Ca(1)–O(1)#3	180.00	O(2)#1–Ca(1)–O(2)#4	180.00	C(1)–N(4)–N(3)	105.20(19)
O(1)–Ca(1)–O(3)#3	93.13(6)	O(1)#3–Ca(1)–O(3)#3	86.87(6)	N(4)–C(1)–N(1)	109.4(2)
O(1)–Ca(1)–O(2)#4	89.53(5)	O(1)#3–Ca(1)–O(2)#4	90.47(5)	N(1)–C(2)–C(3)	113.34(18)
O(2)#1–Ca(1)–O(3)	87.05(6)	O(2)#4–Ca(1)–O(3)#3	87.05(6)	O(2)–C(3)–O(1)	125.95(19)
O(1)#3–Ca(1)–O(3)	93.13(6)	C(1)–N(1)–N(2)	108.27(19)	O(2)–C(3)–C(2)	118.57(18)
O(3)–Ca(1)–O(3)#3	180.00	C(1)–N(1)–C(2)	129.6(2)	O(1)–C(3)–C(2)	115.46(18)
O(2)#1–Ca(1)–O(3)	92.95(6)	N(2)–N(1)–C(2)	122.10(19)		

Symmetry transformations used to generate equivalent atoms for $[Ca(tza)_2(H_2O)_2]_n$, bond lengths, (#1): $1-x$, $-1/2+y$, $1/2-z$; (#2): $1-x$, $1-y$, $-z$; (#3): x, $3/2-y$, $-1/2+z$; bond angles, (#1): $1-x$, $-1/2+y$, $1/2-z$; (#2): $1-x$, $1/2+y$, $1/2-z$; (#3): $1-x$, $1-y$, $-z$; (#4): x, $3/2-y$, $-1/2+z$.

3. Results and discussion

3.1. *Structural description of* $[Ca(tza)_2(H_2O)_2]_n$

The crystal of $[Ca(tza)_2(H_2O)_2]_n$ belongs to the monoclinic system, $P2(1)/c$ space group, $a = 9.352(3)$ Å, $b = 7.293(2)$ Å, $c = 9.922(3)$ Å, $\beta = 106.198(4)°$, $V = 649.9(4)$ Å^3, $Z = 2$. The coordination environment of calcium and the molecular structure of $[Ca(tza)_2(H_2O)_2]_n$ with atom labeling are shown in figure 2. Selected bond lengths and angles for $[Ca(tza)_2(H_2O)_2]_n$ are given in table 2. The hydrogen bond lengths and angles are listed in table 3.

Structure analysis shows that the asymmetric unit of $[Ca(tza)_2(H_2O)_2]_n$ is comprised of one central Ca(II), two tza ions ,and two coordinated water molecules. The central Ca(II) is coordinated by six oxygens, four of which are from four different tza ions and other two are from water. The Ca–O(tza) bond lengths between Ca(II) and tza ions are 2.279(2), 2.282(2), 2.279(2) and 2.282(2) Å, respectively, with an average of 2.2805 Å. The lengths of Ca–O(H_2O) between Ca(II) and water are 2.403(2) Å, about 0.12 Å longer than Ca–O (tza). The angles formed by Ca(II) and two adjacent oxygens are close to 90°, with a maximum deviation of 3.13°. Trans oxygens and the central Ca(II) are co-linear. The slightly distorted octahedral configuration of the Ca(II) is shown in figure 3.

Carboxylates and nitrogens in the tetrazolyl ring, have good coordination ability. Htza, with both a carboxylate and tetrazolyl ring, is a multidentate ligand with several coordination modes. In this compound, nitrogens of the tetrazolyl ring do not coordinate to calcium and

Table 3. Selected hydrogen bonds for $[Ca(tza)_2(H_2O)_2]_n$ (distances in angstrom, angles in deg).

D–H···A	D–H (Å)	H···A (Å)	D–A (Å)	D–H···A (°)
O(3)–H(3A)···N(3)#1	0.77(3)	2.19(3)	2.957(3)	174(4)
O(3)–H(3B)···N(4)#2	0.88(4)	2.01(4)	2.870(3)	167(4)
C(1)–H(1)···O(1)#2	0.9500	2.5800	3.365(3)	140.00
C(1)–H(1)···O(2)#2	0.9500	2.2700	3.183(3)	162.00

Symmetry transformations used to generate equivalent atoms for $[Ca(tza)_2(H_2O)_2]_n$, (#1): $-1+x$, y, $-1+z$; (#2): $1-x$, $1-y$, $1-z$.

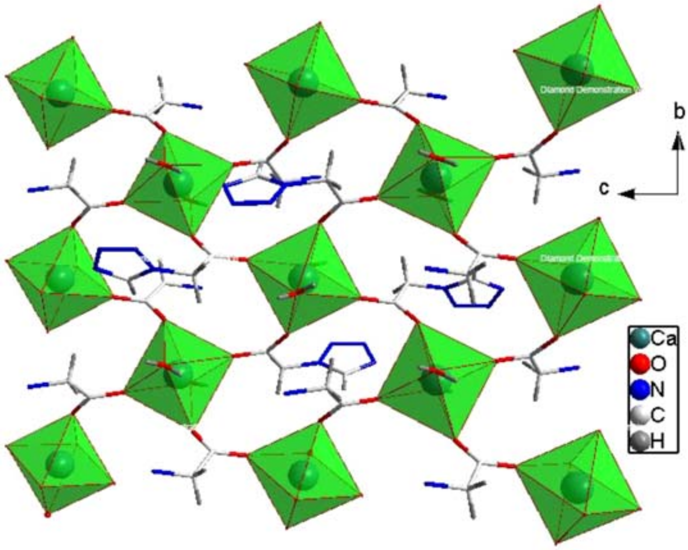


Figure 3. Slightly distorted octahedron of calcium coordinated by four tza^- ions and two waters.

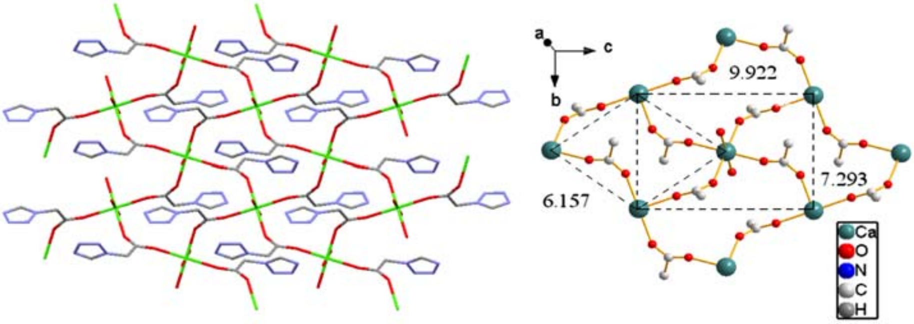


Figure 4. The 2-D layer of $[Ca(tza)_2(H_2O)_2]_n$ formed by bridging tza^- connecting two adjacent Ca ions in the *bc* plane.

the structure is constructed by carboxylic oxygens. Bidentate tza join two adjacent Ca(II) ions through carboxylate oxygen. As shown in figure 4, the 2-D supramolecular laminar structure of $[Ca(tza)_2(H_2O)_2]_n$ was formed via four bridging tza ions connecting one Ca(II) with four adjacent Ca(II) ions. The layers extending along the *bc* plane are separated by 9.352 Å, equal to the unit cell parameter a. The distances between two calciums (Ca···Ca) along *b* and *c* are 7.293 and 9.922 Å, equal to the unit cell parameters *b* and *c*. Four adjacent calciums are connected in a rhombic structure by carboxylates through Ca–O1, 2.279 Å and Ca–O2, 2.282 Å. The rhomboidal geometry repeats itself to form the 2-D laminar structure. The laminar structure of $[Ca(tza)_2(H_2O)_2]_n$ is similar to $[Cu(tza)_2]_n$, in which tza is coordinated with one nitrogen of tetrazolyl ring and one carboxylate O [22,24].

Figures 5 and 6 are the packing diagrams of $[Ca(tza)_2(H_2O)_2]_n$ viewed along the b-axis and c-axis, respectively. Many hydrogen bonds link the layers into a 3-D network.

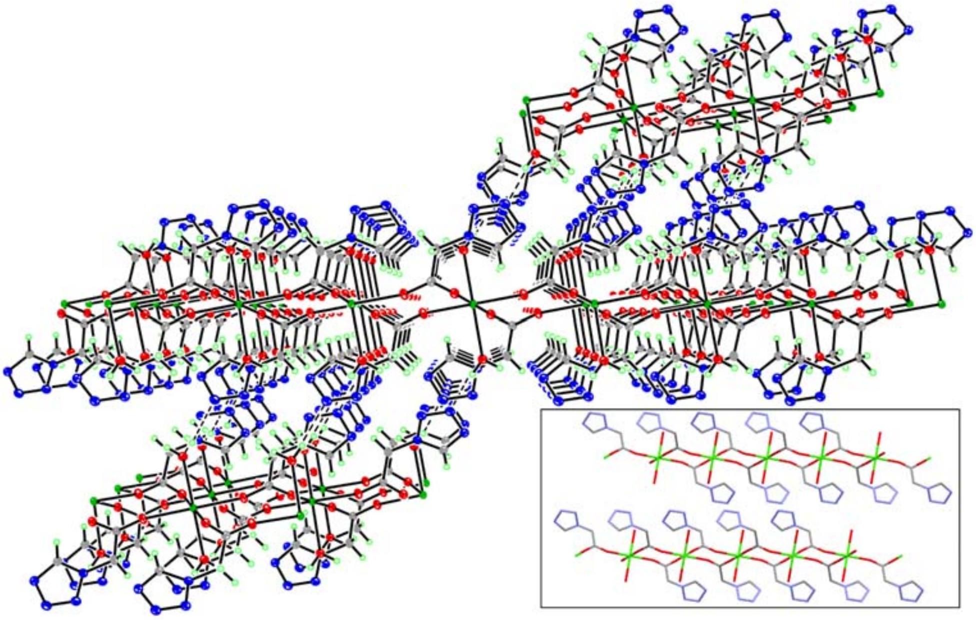


Figure 5. Packing diagram of $[Ca(tza)_2(H_2O)_2]_n$ viewed along the *b*-axis.

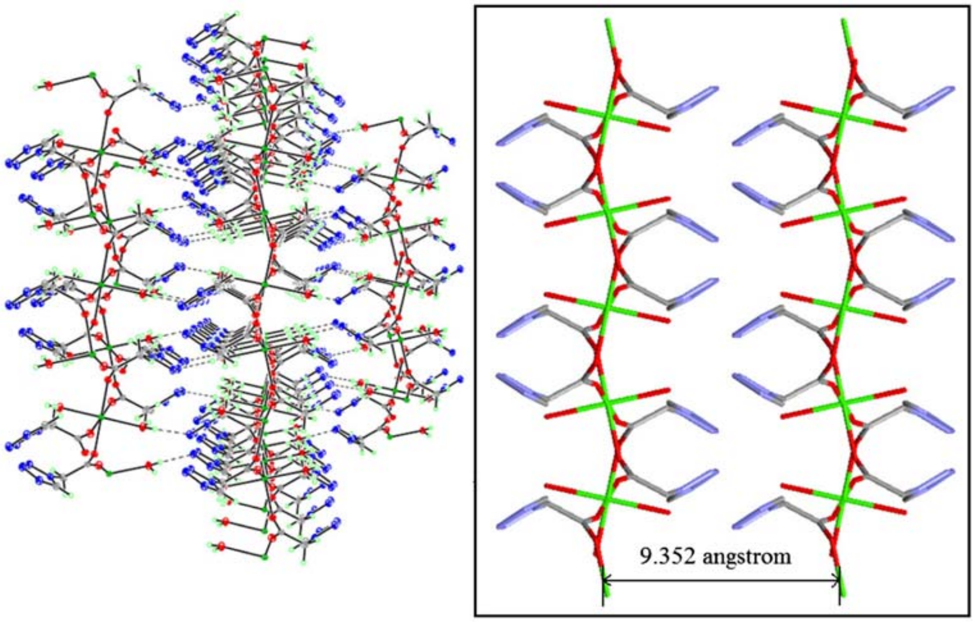


Figure 6. Packing diagram of $[Ca(tza)_2(H_2O)_2]_n$ viewed along the *c*-axis.

Coordinated water provides an intralayer hydrogen bond (O(3)···N(4), 2.870 Å) to N of the tetrazolyl ring to consolidate the layer structure. Another hydrogen bond connects the layers through water via hydrogen bonds (O(3)···N(3), 2.957 Å) to nitrogen of the tetrazolyl ring. Hydrogen-bonding interactions and electrostatic forces make important contributions to the stability.

3.2. *Thermal decomposition*

To assess the thermal stability of the title compound, the thermal decomposition was investigated by DSC and TGA measurements. The DSC and TG-DTG curves of $[Ca(tza)_2(H_2O)_2]_n$ under linear heating rate of 10 °C min^{-1} are shown in figures 7 and 8. The tested samples were dried in a water bath at 50 °C to remove any moisture in the crystal, but not coordinated water.

In the DSC curve, there are one endothermic peak and one sharp exothermic peak. The endothermic process occurs at 128–156 °C, with peak temperature of 144 °C. In the TG-DTG curves, mass loss of 10% confirmed dehydration with a theoretical mass loss of two waters (10.9%). The absorption band at 3446 cm^{-1} in the FT–IR spectra of the residue of $[Ca(tza)_2(H_2O)_2]_n$ obtained after dehydration also disappeared.

The intense exothermic process of $[Ca(tza)_2(H_2O)_2]_n$ is at 282–333 °C with peak temperature of 302 °C. Contrasting with Cu [41], K [28], Bi [27] and Pb [26] complexes of tza, $[Ca(tza)_2(H_2O)_2]_n$ is more thermally stable; the onset temperatures of the four complexes are 183, 192, 217, and 228 °C, respectively. The drastic exothermic decomposition of $[Ca(tza)_2(H_2O)_2]_n$ can be ascribed to collapse of the complex. Corresponding to the mass loss in the TG–DTG curves, a great amount of gas is generated. The mass of the final residue at 600 °C is 33% of the initial mass, which nearly coincides with the calculated value of $CaCO_3$ (30%). The absorption band of the residue at 600 °C also proved that the final residue is $CaCO_3$.

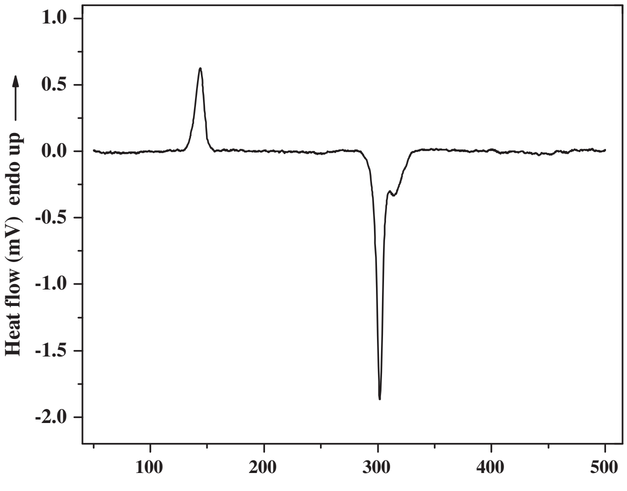


Figure 7. DSC curve of $[Ca(tza)_2(H_2O)_2]_n$ at a heating rate of 10 °C min^{-1}.

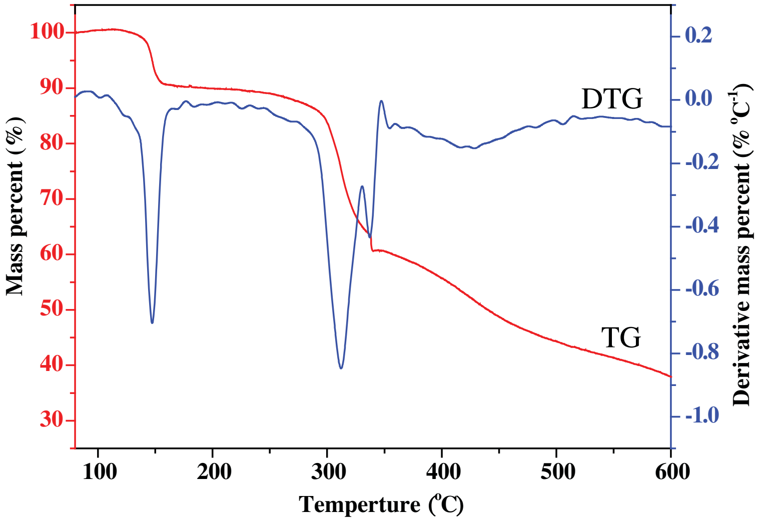


Figure 8. TG-DTG curves of $[Ca(tza)_2(H_2O)_2]_n$ at a heating rate of 10 °C min^{-1}.

3.3. *Calculation of critical temperature of thermal explosion, $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$*

The value of the peak temperature of the exothermic step of $[Ca(tza)_2(H_2O)_2]_n$ corresponding to $\beta \to 0$ obtained according to the following equation [42] is 563 K, where b and c are coefficients.

$$T_{pi} = T_{p0} + b\beta_i + c\beta_i^2$$

The corresponding critical temperature of thermal explosion (T_{bp}) obtained from the following equation is 574 K, where R is the gas constant and E_O is the value of E_a by Ozawa's method.

$$T_{bp} = \frac{E_O - \sqrt{E_O^2 - 4E_O R T_{p0}}}{2R}$$

The entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$), and free energy of activation ($\Delta G^{\neq}$) of the exothermic decomposition reaction of $[Ca(tza)_2(H_2O)_2]_n$ corresponding to $T = T_{p0}$, $E_a = E_K$, and $A = A_K$ obtained by the following equations [43–46] are -67.62 J mol^{-1} K^{-1}, 257.52 kJ mol^{-1} and 295.59 kJ mol^{-1}, respectively.

$$\begin{gathered} A = \tfrac{k_B T}{h} e^{\Delta S^{\neq}/R} \\ \Delta H^{\neq} = E_a - RT \\ \Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \end{gathered} \qquad (1)$$

where k_B is the Boltzmann constant (1.3807×10^{-23} J K^{-1}) and h is the Plank constant (6.626×10^{-34} J s^{-1}).

4. Conclusion

A new polymeric calcium compound with Htza was prepared and characterized. $[Ca(tza)_2(H_2O)_2]_n$ belongs to the monoclinic system, $P2(1)/c$ space group, $a = 9.352(3)$ Å, $b = 7.293(2)$ Å, $c = 9.922(3)$ Å, $\beta = 106.198(4)°$, $V = 649.9(4)$ Å^3, $Z = 2$. Calcium is coordinated to a slightly distorted octahedron by four carboxylic oxygens and two water oxygens. A layer structure is formed in the *bc* plane by the bridging tza connecting adjacent Ca(II) centers. With the heating rate of 10 °C min^{-1}, the two coordinated water molecules were lost at 128 °C and decomposition of $[Ca(tza)_2(H_2O)_2]_n$ starts at 282 °C with a sharp exothermic peak. The thermal parameters E_a, $\ln A$, T_{p0}, T_{bp}, $\Delta S^{\neq}$, $\Delta H^{\neq}$, and $\Delta G^{\neq}$ were obtained by non-isothermal kinetic analysis and the Arrhenius equation of the exothermic step of $[Ca(tza)_2(H_2O)_2]_n$ can be expressed as $\ln k = 21.96–262.2 \times 10^3/RT$.

Supplementary material

CCDC 783871 contains the supplementary crystallographic data of $[Ca(tza)_2(H_2O)_2]_n$. These data can also be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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