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CRYSTAL STRUCTURE AND THERMAL ANALYSIS OF DIAQUADI (1,2,4-TRIAZOL-5-ONE)ZINC(II) ION NITRATE

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A new complex, diaquadi(1,2,4-triazol-5-one)zinc(II) ion nitrate formulated as $\{[Zn(TO)_2(H_2O)_2](NO_3)_2\}_n$ (**1**) (1,2,4-triazole-5-one, abbreviated as: TO) was synthesized and characterized by elemental analysis, X-ray single crystal diffraction, infrared spectrum (IR), differential scanning calorimetry (DSC), thermogravimetric analysis and differential thermogravimetric analysis (TG-DTG). The X-ray structure analysis reveals that the complex is orthorhombic with space group Pbca and unit-cell parameters a=6.9504(2) Å; b=10.6473(3) Å; c=17.8555(5) Å. Based on the result of thermal analysis, the thermal decomposition process of the compound was derived. From measurement of the enthalpy of solution in water in 298.15 K, the standard molar enthalpy of solution of lignand TO and the complex were determined as 15.43±0.18 and 52.64±0.42 kJ mol^{-1}, respectively. In addition, the standard molar enthalpy of formation of TO(aq) was calculated as –126.97±0.72 kJ mol^{-1}.

Keywords: *crystal structure, standard enthalpy of solution, thermal analysis, 1,2,4-triazole-5-one (TO), zinc complex*

Introduction

High-nitrogen metal compounds can be used as burning rate modifiers that are important components of solid propellants. Conventional double base propellants often utilize lead-based compounds as component of burning rate modifiers, which are hazardous to environment and personnel in the workplace. Many attentions were paid to find eco-friendly burning rate modifiers [1–4]. The metal complexes with 1,2,4-triazole derivatives because of high nitrogen composition, high enthalpy of formation and high densities are candidates to fulfill this purpose [5, 6]. 3-Nitro-1,2,4-triazol-5-one (NTO) complexes have been found that, when they are added to a formula system, the burning velocity and specific impulse are greatly improved, while the index of pressure decreases [7–11]. As high nitrogen compounds, the metal complexes with 1,2,4-triazole-5-one may have the potential uses as burning rate modifiers, however, only a few researches were focused on 1,2,4-triazol-5-one (TO) complexes [12–14]. In order to provide theoretic example for the further application, we are exploring the synthesis, structure characteristics and thermal decomposition processes of TO transition metal compounds.

In this paper, a new TO complex of zinc, diaquadi(1,2,4-triazol-5-one)zinc(II) ion nitrate formulated as $\{[Zn(TO)_2(H_2O)_2](NO_3)_2\}_n$ (**1**) (1,2,4-triazole-5-one, abbreviated as: TO), has been synthesized and structurally characterized. In addition, elemental analysis, IR, DSC, TG-DTG were presented. The thermal decomposition process for complex was derived. Additionally, the standard molar enthalpy of solution of the ligand and the complex were measured using a RD496-III-type microcalorimeter.

Experimental

Preparation of the complex

According to the literature method, formic acid (88%, Xi’an Chemical Co.) and semicarbazide hydrochloride (99%, ACROS) were used to synthesize 1,2,4-triazole-5-one (TO), and the *m.p.* is 234.04°C which accorded with [15, 16].

$Zn(NO_3)_2{\cdot}6H_2O$ (AR) was available commercially and used without further purification.

An appropriate amount of TO (1 mmol, 0.085 g) was dissolved in water (5 mL), and was dropped into an ethanol solution (15 mL) of zinc nitrate (0.5 mmol, 0.149 g) at 60°C. The mixed solution was stirred for about 30 min to get white precipitates. After it has been leached, the filtrate was left at the room temperature for 20 days to obtain the white single crystal for X-ray measurement. The white precipitates were washed with anhydrous alcohol for 3 times and dried at room temperature for further analysis (0.125 g, 63% yield based on zinc nitrate).

$$Zn(NO_3)_2{\cdot}6H_2O+2TO(1,2,4\text{-triazole-5-one})\xrightarrow{60℃}[Zn(TO)_2(H_2O)_2](NO_3)_2+4H_2O$$

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Table 1 Crystallographic data for the compound $\{[Zn(TO)_2(H_2O)_2](NO_3)_2\}_n$

Empirical formula	$C_4H_{10}N_8O_{10}Zn$
Formula mass/mg	395.57
Crystal size/mm	0.22×0.17×0.14
Crystal system	orthorhombic
Temperature/K	296(2)
Wavelength/Å	0.71073
Space group	Pbca
a/Å	6.9504(2)
b/Å	10.6473(3)
c/Å	17.8555(5)
V/Å^3	1321.36(6)
Z	4
D_c/mg m^{-3}	1.988
F (000)	800
θ range for data collection/°	3.68–27.89
Absorption coefficient/mm^{-1}	1.936
Limiting indices	$-9\le h\le 8$, $-13\le k\le 14$, $-23\le l\le 23$
Completeness to θ=27.89	99.6%
Refinement method	full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.027
Reflections collected/unique	7520/1569 [*R*(int)=0.0293]
Final *R* indices [$I>2\sigma(I)$]	R1=0.0268, wR2=0.0751
R indices (all data)	R1=0.0398, wR2=0.0797
Largest diff. peak and hole/e Å^{-3}	0.410 and –0.262

Instrumentations

C, H, N contents were determined on a Perkin-Elmer 2400 type elemental analyzer. Zn^{2+} was titrated with ethylenediamine tetraacetic acid (EDTA). IR spectrum was derived by a Nicolet 60 SXR FT-IR (Nicolet, USA) spectrometer in the 4000–400 cm^{-1} regions (KBr pellets). The DSC experiments were performed with CDR-4P thermal analyzer (Shanghai Balance Instrumental Company). The purge gas was N_2 with the flowing rate 60 mL min^{-1} and the heating rate was 10°C min^{-1} with samples weighing 1.23 mg.

All TG-DTG tests were performed with a Perkin-Elmer thermogravimetric instrument. The purge gas was N_2 flowing of 60 mL min^{-1}. A heating rate of 10°C min^{-1} was adopted, with samples weighing 0.9690 mg. All single crystal X-ray experiments were performed on a Bruker Smart-1000CCD diffractometer with graphite monochromated MoK_α radiation (λ=0.71073 Å). The single crystal structure of complex was solved by direct methods using SHELXS-97 [17] and all non-H atoms were located using subsequent Fourier-difference methods. Non-hydrogen atoms were refined anistropically. The hydrogen atoms of the organic ligands were generated geometrically.

The calorimetric experiments were performed with an RD496-type microcalorimeter [18]. The calorimetric constant at 25.15°C was determined by the Joule effect before experiment, which is 63.901±0.030 μV mW^{-1}. The enthalpy of dissolution of KCl (spectral purity) in deionized water was measured to be 17.238±0.048 kJ mol^{-1}, which was in good agreement with the value of 17.241±0.018 kJ mol^{-1} from [19]. The accuracy was 0.02% and the precision was 0.3%, which indicates that the calorimetric system is accurate and reliable.

Results and discussion

Fig. 2 The alternate linkage of Zn(II) and TO ligand

Elemental analysis

Anal. calcd for $ZnC_4H_{10}N_8O_{10}$: C, 12.15%; H, 2.55%; N, 28.33%; found: C, 12.43%; H, 2.126%; N, 28.41%.

Infrared spectrum

In the IR spectrum of the complex, the strong and broad peak at 3155 cm^{-1} is assigned to the stretching vibration of hydroxyl (ν_{O-H}), which is not found in the IR spectrum of the ligand, indicating the presence of water molecular in the compound. The appearance of striking peaks at 1388 cm^{-1} can be attributed to the stretching vibrations of nitrate radical and deformation vibration of nitrate radical appears at 816 cm^{-1}. The $\nu_{C=N}$ at 1568 cm^{-1} have shifted towards higher wave number compared with the ligand and the characteristic stretching vibration of C=O is found at 1766 cm^{-1}, which shifted 70 cm^{-1} to higher wave number compared to the ligand TO (1696 cm^{-1}). The shifts could be ascribed to the coordination interaction with metal ion, which has been verified by X-ray single crystal analysis. The peaks at 956, 711, 508 cm^{-1} are assigned to the deformation vibrations of the framework of triazolone [12, 13] and ν_{C-H} appeared at 2844 cm^{-1}.

Structure analysis

As shown in Fig. 1, the Zn(II) shows a typical octahedral central symmetrical geometry and the Zn(II) is at the center of the molecule. The Zn(II) is coordinated by two nitrogen and two oxygen atoms from four TO ligands in equatorial plane, and two axial oxygen atoms from coordinated water molecules. Selected bond lengths and angles are shown in Table 2. As shown in

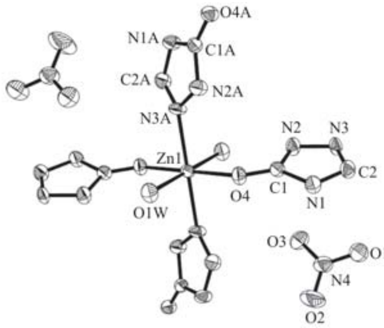

Fig. 1 Coordination environment of Zn(II) in compound $\{[Zn(TO)_2(H_2O)_2](NO_3)_2\}_n$ with 50% thermal ellipsoid probability

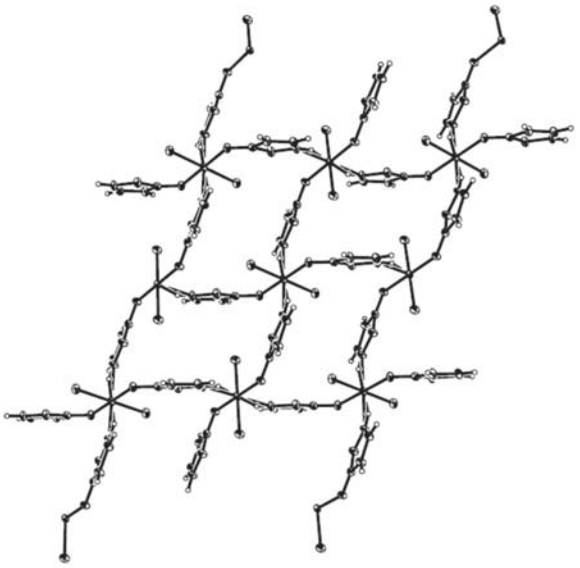

Fig. 2 View of the two dimensional structure of the complex

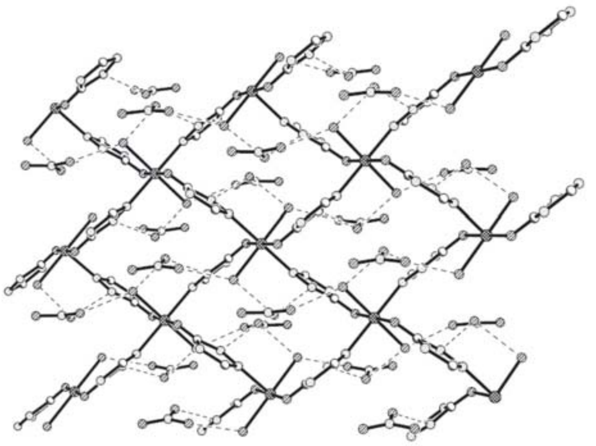

Fig. 3 Packing arrangement and the hydrogen bond of $[Zn(TO)_2(H_2O)_2]_2(NO_3)_2$

through the coordinated atoms O_4 and N_3 generates a two-dimensional plane with (4,4) topology structure. Within the (4,4) topological layer, the four connected nodes are provided by Zn(II) ions while the connecters are TO ligands, and the direction of TO ligands paralleled within each (4,4) lattice are opposed with each other. There are two nitrate radicals in each (4,4) lattice, which connect with other atoms through hydrogen bonds as Fig. 3 has shown. Hydrogen bond distance and angles are shown in Table 3. Hydrogen bonds together with the two-dimensional layer form the three-dimensional network of $\{[Zn(TO)_2(H_2O)_2](NO_3)_2\}_n$.

Thermal analysis

DSC and TG-DTG curves are shown in Figs 4–6.

According to the TG-DTG curve, the decomposition process of the compound can be divided into

Table 2 Selected bond lengths (Å) and bond angles (°)

Zn(1)–N(3)^{i}	2.0920(2)	C(2)–N(3)	1.286(2)
Zn(1)–O(4)	2.0949(1)	C(2)–N(1)	1.346(2)
Zn(1)–O(1W)	2.1695(1)	N(2)–N(3)	1.376(2)
C(1)–O(4)	1.246(2)	C(1)–N(2)	1.333(2)
C(1)–N(1)	1.364(2)		
N(3)^{i}–Zn(1)–N(3)^{ii}	180.00(7)	O(4)–Zn(1)–O(4)^{iii}	180.00(7)
N(3)^{ii}–Zn(1)–O(4)	91.84(5)	N(3)^{i}–Zn(1)–O(1W)	89.05(6)
N(3)^{i}–Zn(1)–O(4)	88.16(5)	N(3)^{ii}–Zn(1)–O(1W)	90.95(7)
O(1W)–Zn(1)–O(1W)^{iii}	180.00(0)	N(3)–C(2)–N(1)	111.35(2)
O(4)–Zn(1)–O(1W)	84.50(5)	C(2)–N(1)–C(1)	108.25(1)
O(4)^{iii}–Zn(1)–O(1W)	95.50(5)	C(1)–N(2)–N(3)	111.82(1)
N(2)–C(1)–N(1)	103.96(2)	C(2)–N(2)–N(2)	104.62(1)
C(2)–N(3)–Zn(1)^{iv}	130.84(1)	N(2)–N(3)–Zn(1)^{iv}	122.17(1)
C(1)–O(4)–Zn(1)	130.73(1)		

Symmetry codes: ^{i}–x+3/2, y+1/2, z; ^{ii}x+1/2, –y+1/2, –z; ^{iii}–x+2, –y+1, –z; ^{iv}x–1/2, –y+1/2, –z

Table 3 Hydrogen bond distance (Å) and angles (°) of complex (**1**)

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
O(1W)–H(1WB)···O(1)^{i}	0.78(3)	2.05(3)	2.823(2)	170(3)
O(1W)–H(1WA)···O(2)^{ii}	0.88(3)	1.95(3)	2.825(2)	168(2)
N(2)–H(3)···O(1W)^{iii}	0.92(3)	2.37(3)	2.954(2)	121(2)
N(2)–H(3)···O(2)^{iv}	0.92(3)	2.09(3)	2.852(2)	140(3)
N(1)–H(1)···O(1)^{v}	0.86(0)	1.97(0)	2.784(1)	158(1)

Symmetry codes: ^{i}–x+3/2, y+1/2, z; ^{ii}x+1, y, z; ^{iii}–x+2, –y+1, –z; ^{iv}x+1/2, –y+1/2, –z; ^{v}x+1/2, y, –z+1/2

two steps. The first step in the range of 140 to 178°C is confirmed as the loss of coordinated water and the break of the triazole ring, which is similar with that of the complex $\{[Cu(TO)_2(H_2O)_2](NO_3)_2\}_n$. Compared with IR spectrum of the title complex, the disappearance of the vibrations at 3155, 2844, 1766, 956, 711 and 508 cm^{-1} in the IR spectrum of the residual proves that the complex is firstly thermodecomposed as $Zn(NO_3)_2$ when the experimental mass loss well accords with the calculate value 47.88%. In the second step, the IR spectrum of the residue after 700°C shows a strong absorption peak at 475 cm^{-1}, which is assigned to that of ZnO. The residual amount of 20.03% is in good agreement with the calculated amount of 20.47%. Different with the title complex, the similar compound $\{[Cu(TO)_2(H_2O)_2](NO_3)_2\}_n$ was finally thermolysed as $Cu(CN)_2$ and CuO at 242°C. According to above analysis, the decomposition processes of the title complex can be expressed as follows:

$$\{[Zn(TO)_2(H_2O)_2](NO_3)_2\}_n \xrightarrow{140\text{–}178℃} Zn(NO_3)_2\ (47.88\%) \xrightarrow{180\text{–}568℃} ZnO\ (20.03\%)$$

In the DSC curve of the ligand TO, the melting point is 234.04°C and the decomposition process is immediately after the melting process of the ligand. The two processes are endothermic, which are quite different with the DSC curve of the complex. It is obvious that there are two stages in the DSC curve of the complex in the range of 140 to 178°C as Fig. 6 has shown. The first endothermic process is considered as the dehydration of coordinated water. As shown in Fig. 3 and Table 3, hydrogen bonds formed between water and nitrate fix the uncoordinated nitrate in the (4,4) lattice, and the formation of the hydrogen bonds have significant effect on the density, stability of the complex. It was reported that the formation of hydrogen bonds could decrease the shock sensitivity while the overall lattice stability increases [20–22]. As Figs 4 and 6 indicated, the complex decomposes drastically after losing coordination water molecules while the break of the triazole ring and the break of the coordination bonds with the metal. Although the decomposition process of

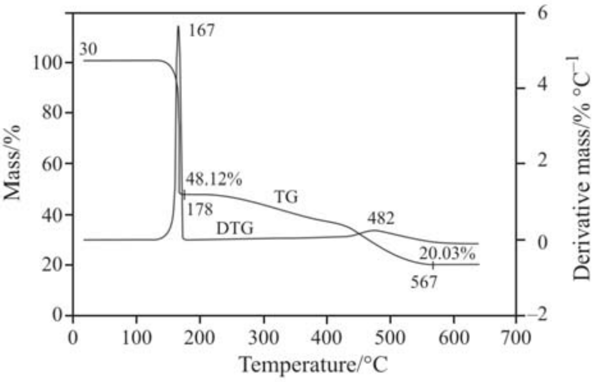

Fig. 4 TG-DTG curves of the complex $\{[Zn(TO)_2(H_2O)_2](NO_3)_2\}_n$

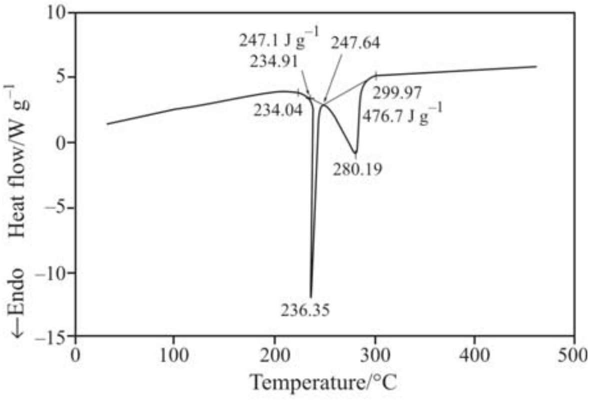

Fig. 5 DSC curve of the ligand TO in the temperature range 50 to 450°C

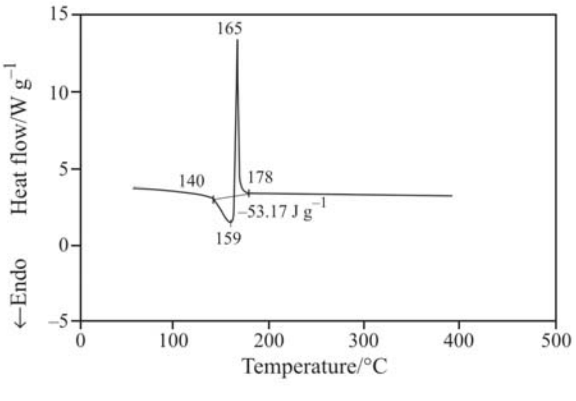

Fig. 6 DSC curve of the complex $[Zn(TO)_2(H_2O)_2](NO_3)_2$ in the temperature range 50 to 400°C

Table 4 Data of the standard molar enthalpy of solution of the ligand and the complex

TO (1,2,4-triazole-5-one)			$\{[Zn(TO)_2(H_2O)_2](NO_3)_2\}_n$		
m/mg	Q/mJ	$\Delta_{sol}H_m^\theta$/kJ mol^{-1}	m/mg	Q/mJ	$\Delta_{sol}H_m^\theta$/kJ mol^{-1}
7.72	1413.187	15.56	16.42	2192.284	52.81
6.75	1162.673	14.64	15.97	2169.330	53.73
8.20	1495.977	15.51	14.82	1938.248	51.73
7.63	1435.475	15.99	17.10	2225.297	51.48
6.54	1200.295	15.60	16.85	2298.797	53.96
7.70	1385.840	15.30	15.48	2042.131	52.18
$\Delta_{sol}H_m^\theta$=15.43±0.18 kJ mol^{-1}			$\Delta_{sol}H_m^\theta$=52.65±0.42 kJ mol^{-1}		

the ligand TO is endothermic, the break of the coordination bonds provide enough energy to offset the endothermic energy of the decomposition of the ligand, eventually, the second step of the DSC curve exhibit exothermic character of the complex in the temperature 140~178°C and the ΔH=–53.17 J g^{-1}.

Measurement of the standard molar enthalpy of solution in water at 298.15 K

The standard molar enthalpies of solution of TO and the complex in deionized water at 298.15 K were determined using an RD496-III-microcalorimeter [18], the molar ratio $n(H_2O)/n(\{[Zn(TO)_2(H_2O)_2](NO_3)_2\}_n)$ is 10281–11862, the molar ratio $n(H_2O)/n(TO)$ is 4607–5776. Therefore, the mean of $\Delta_{sol}H_m^\theta$ could be considered an infinite dilution. Data of the standard molar enthalpy of solution of the ligand (TO) and the complex $\{[Zn(TO)_2(H_2O)_2](NO_3)_2\}_n$ are shown in Table 4.

In addition, the enthalpy of formation of TO(aq) can be calculated according to Eq. (1):

$$\Delta_f H_m^\theta\ (TO(aq))= \Delta_{sol} H_m^\theta (TO(Cr))+\Delta_f H_m^\theta\ (TO(Cr)) \qquad (1)$$

where $\Delta_f H_m^\theta$ (TO(Cr))=–142.4±0.70 kJ mol^{-1} [23], so $\Delta_f H_m^\theta$ (TO(aq))=–126.97±0.72 kJ mol^{-1}.

Conclusions

The single crystal of the title complex was prepared in the mixed solvents of water and ethanol. Single crystal X-ray diffraction reveals that TO as a bidentate ligand coordinates with zinc cation, as a result, a typical octahedral geometry of the complex is generated. The complex is thermodecomposed in two steps. The standard molar enthalpies of solution of ligand TO and the complex, the standard molar enthalpy of formation of TO(aq) were determined as 15.43±0.18, 52.64±0.42, –126.97±0.72 kJ mol^{-1}, respectively. These thermochemical analyses provide the theoretic data for the further application of the title complex in the area of energetic material.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 294678. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: t44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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