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Synthesis, Crystal structures, and Thermal behaviors of MBTO·nPhen with M=Co, Ni, Cu, Zn and Phen=1,10-Phenanthroline

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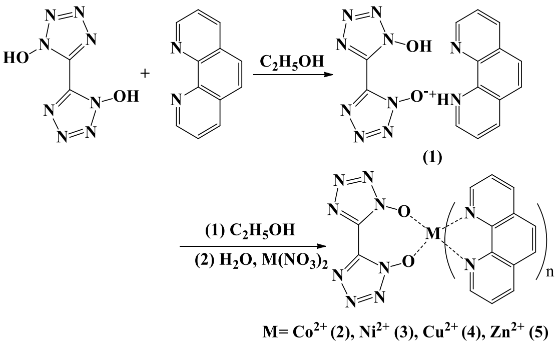
Abstract The cocrystal of 1,10-phenanthrolin-1-ium 1-hydroxy-[5,5'-bitetrazol]-1'-olate (BTO·Phen) from 5,5′-bistetrazole-1,1′-diol dehydrate (BTO) and 1,10-Phenanthroline (Phen) was synthesized in a simple, straightforward manner and was characterized by IR, elemental analysis, and single-crystal X-ray diffraction of several salts (Ni^{2+} and Zn^{2+}) were also given. The X-ray structures show that in the title compounds, the metal atoms are bonded to the nitrogen atom in the Phen ring and the oxygen atom in the bistetrazole ring to form the sandwich structure. Thermal stabilities of all title compounds were determined with Differential scanning Calorimetry (DSC), showing good thermostability. In addition, thermokinetic parameters including the apparent activation energies (E_K and E_O) and pre-exponential factor (A) were also calculated.

Keywords BTO·Phen · Crystal Structure · Thermal behaviors · Thermokinetic parameters

Introduction

5,5′-Bistetrazole-1,1′-diolate dihydroxylammonium (TKX-50) has been proved as high-energy density compound (HEDC) and having good stability [1–4], and its synthetic precursor 1H,1′H-5,5′-Bistetrazole-1,1′-diol (H_2BTO) is a suitable energetic ligand [5–8]. Since the deprotonated skeleton (BTO^{2-}) have two N-oxide anions [3,4,8], it could coordinate with some oxyphilic metal ions to form potential primary explosives with good environmental friendliness [9–13]. 1,10-Phenanthroline (Phen) is a good π-acceptor ligands due to its pre-organized N atoms and its heterocyclic structures [14,15]. In the previous studies, the intermolecular hydrogen bonds formed between the –NH group and N atom belong to phen molecule of the cocrystal of FOX-7·Phen and ZTO·Phen were reported by Zhu [15] and Ma [16]. Due to the presence of hydroxyl hydrogen atoms in BTO, it can bind with lone pair electron N atoms of Phen tightly at the same time in order to form stable complexes and perform good thermal properties.



Scheme 1 The synthesis of BTO·Phen and MBTO·Phen

Herein, we wish to report a direct preparation method with actual production prospects to green explosives (Compounds 2-5) which based on non-heavy metals cations of Co(II), Ni(II), Cu(II) and Zn(II) and BTO^{2-} anion with Phen. The crystal structures of compounds 3 and 5 have been determined by single crystal X-ray diffraction. Thermal analysis shows that all compounds are stable enough upon 200 ºC, and their thermal decomposition kinetic parameters were also calculated to indicate that they have good thermal properties.

Experiment section

Synthesis

1H,1'H-[5,5′-bistetrazole]-1,1′-diol (BTO) was synthesized according to the method reported by Klapötke TM [1].

1'-hydroxy-1H,1'H-[5,5'-bitetrazol]-1-olate 1,10-Phenanthrolin-1-ium (BTO·Phen, 1). BTO (1.00 g) and 1,10-Phenanthroline (1.06 g) was dissolved in 30 mL of C_2H_5OH, Heated to reflux 30 min, and then cooled to the room temperature. The bright colourless precipitate formed, which was filtered and dried under vacuum, yielding 2.01 g (97.6%). IR (KBr, ν/cm^{-1}): 3496, 3399, 3059, 2739, 2082, 1989, 1635, 1616, 1595, 1544, 1502, 1473, 1450, 1406, 1382, 1318, 1238, 1219, 1191, 1142, 1095,1050, 1004, 957, 884, 858,787, 736, 719 cm^{-1}; Elemental Analysis (%) calcd. for $C_{14}H_{10}N_{10}O_2$ (BTO·Phen, 350.10): C, 48.00; H, 2.88; N, 39.99; found: C, 47.98; H, 2.90; N, 40.00.

Cobalt complex (CoBTO·3Phen) (2). BTO (50.00 mg) and 1,10-Phenanthroline (158.91 mg) was dissolved in 50 mL of C_2H_5OH, Heated to reflux 30 min, and then added the solution of $Co(NO_3)_2·6H_2O$ (85.55 mg) in 5 mL water. The bright yellow precipitate formed after a week, which was filtered and dried under vacuum, yielding 216.0 mg (95.7%). IR (KBr, ν/cm^{-1}): 3414, 3234, 1639, 1618, 1401, 1240, 1178, 1070, 858, 620; Elemental Analysis (%) calcd. for $C_{38}H_{24}NiN_{14}O_2$ (CoBTO·3Phen, 766.16): C, 59.46; H, 3.15; N, 25.55; found: C, 59.48; H, 3.20; N, 25.53.

Nickel complex (NiBTO·3Phen) (3). BTO (50.00 mg) and 1,10-Phenanthroline (158.91 mg) was dissolved in 50 mL of C_2H_5OH, Heated to reflux 30 min, and then added the solution of $Ni(NO_3)_2·6H_2O$ (85.48 mg) in 5 mL water. The bright pink precipitate formed after a week, which was filtered and dried under vacuum, yielding 220.0 mg (97.5%). IR (KBr, ν/cm^{-1}): 3412, 3237, 1618, 1516, 1423, 1402, 1240, 1177, 1070, 988, 848, 725, 626; Elemental Analysis (%) calcd. for $C_{38}H_{24}NiN_{14}O_2$ (NiBTO·3Phen, 766.16): C, 59.48; H, 3.15; N, 25.55; found: C, 59.53; H, 3.19; N, 25.62.

Copper complex (CuBTO·2Phen) (4). BTO (50.00 mg) and 1,10-Phenanthroline (105.95 mg) was dissolved in 50 mL of C_2H_5OH, Heated to reflux 30 min, and then added the solution of $Cu(NO_3)_2·xH_2O$ (55.67 mg) in 5 mL water. The bright green precipitate formed after a week, which was filtered and dried under vacuum, yielding 160.0 mg (97.4%). IR (KBr, ν/cm^{-1}): 3414, 3235, 1629, 1397, 1146, 614; Elemental Analysis (%) calcd. for $C_{26}H_{16}CuN_{12}O_2$ (CuBTO·2Phen, 592.05): C, 52.75; H, 2.72; N, 28.39; found: C, 52.81; H, 2.80; N, 28.43.

Zinc complex $(ZnBTO\cdot 2Phen)_2\cdot C_2H_5OH$ (5). BTO (50.00 mg) and 1,10-Phenanthroline (105.95 mg) was dissolved in 50 mL of C_2H_5OH, Heated to reflux 30 min, and then added the solution of $Zn(NO_3)_2\cdot 6H_2O$ (55.13 mg) in 5 mL water. The bright green precipitate formed after a week, which was filtered and dried under vacuum, yielding 165.0 mg (94.2%). IR (KBr, ν/cm^{-1}): 3413, 3238, 1638, 1618, 1518, 1426, 1249, 1226, 1164, 1103, 849, 767, 725, 624; Elemental Analysis (%) calcd. for $C_{54}H_{38}N_{24}O_5Zn_2$ ($(ZnBTO\cdot 2Phen)_2\cdot C_2H_5OH$, 1230.20): C, 52.57; H, 3.10; N, 27.25; found: C, 52.49; H, 3.12; N, 27.31.

Physical measurements and instrumentations

Infrared spectra were measured with a Bruker Spectrum One FTIR spectrometer. The elemental C, H, and N of title compounds were determined by Vario EL III. Thermal behaviors of title compounds were studied at the heating rates of 5, 10, 15 and 20 °C min^{-1} by using Netsch DSC.

Two irregular crystal of dimension 0.22×0.20×0.18 mm^3 (NiBTO·3Phen) and 0.13×0.12×0.05 mm^3 ($(ZnBTO\cdot 2Phen)_2\cdot C_2H_5OH$) were measured and collected on a Bruker three–circle platform diffractometer equipped with a Bruker-AXS SMART APEX II CCD detector using graphite monochromated MoKa radiation of λ=0.71073 Å. The structure was solved by the direct methods (SHELXTL-97[17,18], DIAMOND 3.2[19]) and refined by the full-matrix-block least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Table 1 shows the results of the crystal structure solution and refinement for compounds 3 and 5. The selected bond distances of title compounds are listed in Supporting Information (Table S1).

Table S1 Crystallographic data and structure refinement details for compounds 2 and 4

Compound	NiBTO·3Phen (3)	$(ZnBTO\cdot 2Phen)_2\cdot C_2H_5OH$ (5)
Formula	$C_{38}H_{24}NiN_{14}O_2$	$C_{54}H_{38}N_{24}O_5Zn_2$
Mw /g mol^{-1}	767.64	1233.82
Crystal system	Triclinic	Monoclinic
Crystal group	$P{-1}$	$P2_1/n$
a/ Å	10.9701(17)	14.426(3)
b/ Å	11.0348(15)	21.533(4)
c/ Å	17.439(2)	18.445(4)
α/°	85.996(4)	90
β/°	73.447(4)	112.44
γ/°	80.876(5)	90
V/ Å^3	1997.3(5)	5296(2)
z	2	4
$\rho_{calc.}$ /g cm^{-3}	1.276	1.547
μ mm^{-1}	0.481	0.982
F(000)	786	2520.0
2θ range /°	2.438 - 50.988	3.076 - 49.998
Temp. /K	296(2)	153(2)
Refl. collected	13137	36087
Refl. unique	7167	9291
R (int)	0.0886	0.0705
Data /rest. /param.	7167/0/496	9291/18/767
GOOF	0.897	1.299
R_1, wR_2 [$I>2\sigma(I)$]	R_1=0.0717, wR_2=0.1501	R_1=0.0910, wR_2=0.2427
R_1, wR_2 (all data)	R_1=0.1589, wR_2=0.1912	R_1=0.1118, wR_2=0.2747
Index range	$-13\le h\le 10$, $-13\le k\le 13$, $-20\le l\le 20$	$-16\le h\le 17$, $-25\le k\le 24$, $-21\le l\le 21$
Largest diff. peak/hole /e Å^{-3}	0.278/–0.302	1.22/–0.99
CCDC	1576747	1585532

Results and Discussion

Crystal Structures of complexes 2 and 4

NiBTO·3Phen (**2**) crystallizes in the triclinic space group *P*-1 with a cell volume of 1997.3(5) Å^3 and two molecules in the unit cell is shown in Fig.1. The crystallographic studies reveal that the symmetric unit is made up of Ni^{2+} cation, BTO^{2-} anion and three coordinated Phen molecules. In crystal structure, Ni(1) is coordinated by three coordinated phenanthroline molecules through six Ni–N [Ni(1)–N(1) = 2.088(5) Å, Ni(1)–N(2) = 2.112(4) Å, Ni(1)–N(3) = 2.071(5) Å, Ni(1)–N(4) = 2.079(5) Å, Ni(1)–N(5) = 2.115(4) Å and Ni(1)–N(6) = 2.074(5) Å]. There is no Ni–N and Ni–O bond between Ni^{2+} and BTO^{2-} anion, which are close to those (Ni–N=2.086(5) and 2.145(6) Å) of [Ni(phen)$_3$]$_2$[Mo$_8$O$_{26}$]·2H$_2$O reported by Wang [20]. In comparison with neutral BTO·Phen, there is slight change on the distances of N–N, C–N, and N–O in the tetrazole ring of BTO^{2-}. The dihedral angles of N(10)–C(37)–C(38)–N(14) (–17.8(12)°) and N(4)–C(1)–C(1)–N(4) (163.3(7)°) indicate that two tetrazole rings are not in one plane.

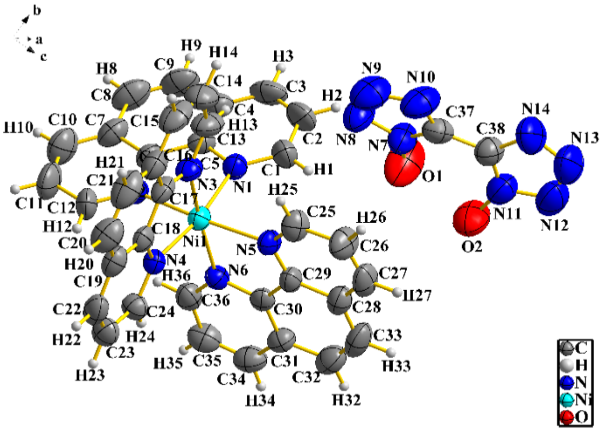


Fig. 2 Crystal structure of NiBTO·3Phen (**2**).

The zinc derivative **4** crystallizes in the monoclinic space group $P2_1/n$ with four molecules in each unit cell, leading to a extremely high density of 1.547 g cm^{-3}, is shown in Fig. 2. The crystallographic studies reveal that Zn center coordinates with two oxygen atoms of BTO^{2-} anion [Zn(1)–O(1) = 2.077(5) Å, Zn(1)–O(2) = 2.117(5) Å, and Zn(2)–O(3) = 2.096(5) Å, Zn(2)–O(4) = 2.080(5) Å], and four nitrogen atoms of two phenanthroline molecules [Zn(1)–N(9) = 2.144(5) Å, Zn(1)–N(10) = 2.142(5) Å, Zn(2)–N(11) = 2.216(6) Å, Zn(2)–N(12) = 2.159(6) Å, and Zn(2)–N(21) = 2.132(6) Å, Zn(2)–N(22) = 2.222(6) Å, Zn(2)–N(23) = 2.134(5) Å, Zn(2)–N(24) = 2.144(6) Å], which are close to those (Zn–N= 2.11 Å and Zn–O =2.09 Å) of [Zn(BTO)·2H$_2$O]$_n$ reported by Zhang [8]. The dihedral angles of N(1)–C(1)–C(2)–N(5) (55.0(11)°), N(1)–C(1)–C(2)–N(8) (–120.5(9)°), N(17)–C(27)–C(28)–N(13) (128.6(9)°), and N(17)–C(27)–C(28)–N(16) (–57.0(14)°) indicate that the two tetrazole rings are not in one plane.

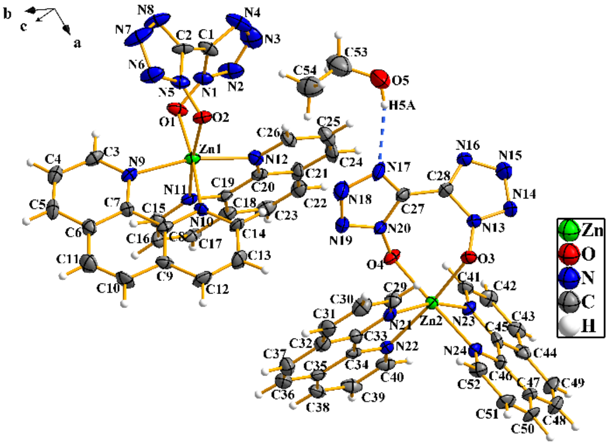


Fig. 2 Crystal structure of ZnBTO·2Phen (**4**).

Thermal behaviors

Figure 3 shows the DSC curves of BTO·Phen and MBTO·nPhen were performed under the linear heating rate of 5 °C·min^{-1}. There is one exothermic peak during the decomposition of the adduct BTO·Phen and CoBTO·3Phen, while one endothermic peak and two exothermic peaks present in the decomposition of NiBTO·3Phen and CuBTO·2Phen. In addition, there are three exothermic peaks occurring at the decomposition of ZnBTO·2Phen. The first exothermic peak temperatures (T_P) of BTO·Phen and MBTO·nPhen salts occurs at 254.2, 269.0, 272.6, 260.0 and 269.1 ºC, respectively; indicating that BTO·Phen and MBTO·nPhen salts are more stable than BTO (231.5 ºC [4,21]).

There is one melting point occurs at 159.5, 152.4 and 165.2 ºC during the decomposition of NiBTO·3Phen, CuBTO·2Phen and ZnBTO·2Phen, respectively. The TG curve (Fig. S3) presented with a mass loss of about 2.95 % ranging from 80 to 123.5 ºC as was found in case of CuBTO·2Phen salt. The mass loss of the first stage is larger than the loss of the two-crystal water component.

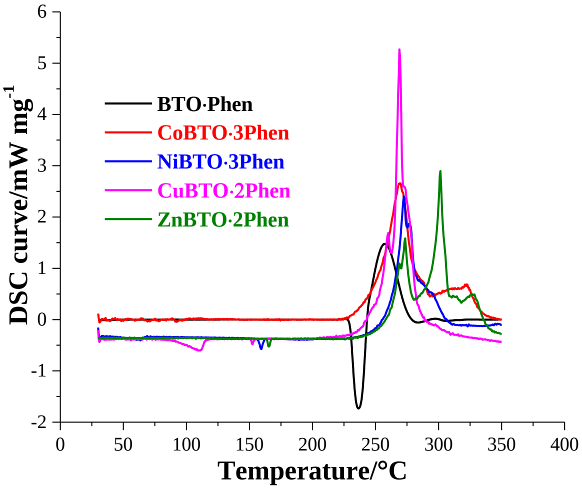


Fig. 3 DSC curve of BTO·Phen and its metal salt at the heating rate of 5 ºC min^{-1}.

Thermokinetic parameters

To determine the kinetic parameters of energetic BTO·Phen and its metal complexes, including the apparent activation energy (E_a) and the pre-exponential factor (A), multi-scan methods of Kissinger [22] and Ozawa [23] would be more suitable to perform in this work [4,24], which were calculated by the following Eqs. (1) and (2).

$$E_a = \frac{R}{0.457}\frac{d(\log\beta)}{d(1/T)} \quad (1)$$

$$-\frac{E_a}{R} = \frac{d(\ln\beta/T_p^2)}{d(1/T_p)} \quad (2)$$

The pre-exponential factor (A) can be calculated from the following equation:

$$A = \frac{\beta \cdot E_a \cdot e^{(E/T_p)}}{R \times T_p^2} \quad (3)$$

The values of the onset temperature (T_{e0}) [25] in the exothermic decomposition stage with the heating rate β close to zero are calculated by Eq (4):

$$T_{ei} = T_{e0} + n\beta_i + m\beta_i^2 (i = 1-4) \quad (4)$$

where n and m are coefficients, i = 1–4. The critical temperatures of thermal explosion (T_b) [26] are calculated by Eq (5):

$$T_b = \frac{E_o - \sqrt{E_o^2 - 4E_oRT_{e0}}}{2R} \quad (5)$$

where E_o is the apparent activation energy calculated using Ozawa's method.

As seen from Table S2, the average E_a of BTO·Phen and its metal complexes are 164.3, 173.7, 193.7, 214.2 and 170.3 kJ mol^{-1}, respectively; which meet in the ordinary range of the thermal decomposition kinetic parameters for energetic materials [27,28]**.** The T_b values of 249.2, 263.1, 264.6, 249.8 and 264.9 ºC are more than BTO (175.4) [21], indicating that the thermodynamically stable sequence was ZnBTO·2Phen>NiBTO·3Phen>CoBTO·3Phen>CuBTO·2Phen>BTO·Phen>BTO.

Conclusion

The cocrystal structure of 1,10-phenanthrolin-1-ium 1-hydroxy-[5,5'-bitetrazol]-1-olate (BTO·Phen) and its metal salts were characterized by single crystal XRD, showing that the two tetrazole ring in BTO^{2-} anion are not in a plane, the Ni atom is coordinated with six N atoms of three Phen molecules, while Zn atom is coordinated with two O atoms of BTO as well as N atoms of two Phen molecules. The average apparent activation energies E_a (164.3, 173.7, 193.7, 214.2 and 170.3 kJ mol^{-1}), pre-exponential factor A (6.772×10^{15}, 1.929×10^{16}, 1.342×10^{18}, 4.463×10^{20} and 8.923×10^{15} s^{-1}) and thermal explosion critical temperatures T_b (249.2, 263.1, 264.6, 249.8 and 264.9 ºC) were calculated by using DSC for BTO·Phen and its complexes, indicating that they have good thermostability.

Acknowledgements

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