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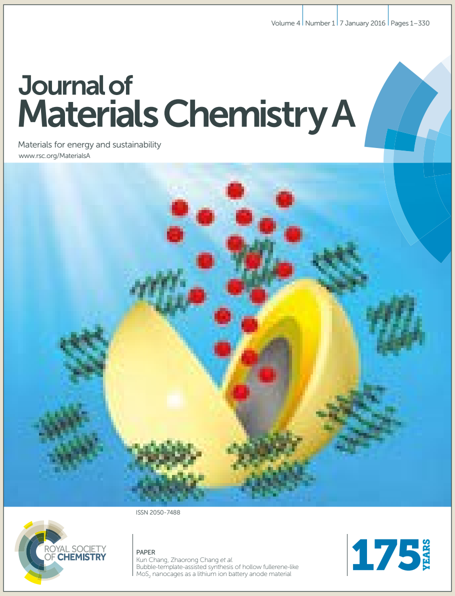

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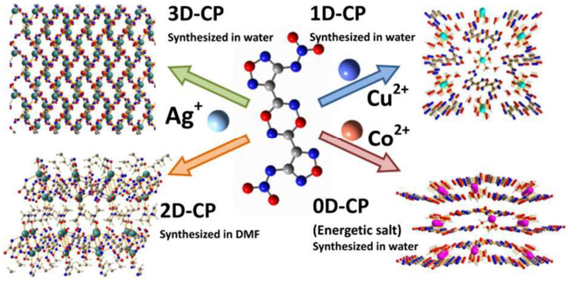

Several high-energy coordination polymers, $\{Ag_2(BNOD)(DMF)_2\}_n$ (1) (2D), $\{Ag_2(BNOD)\}_n$ (1a) (3D), $\{Cu(BNOD)(H_2O)_6\}_n$ (2) (1D), and $Co(BNOD)(H_2O)_6$ (3) (0D energetic salt) have been studied with outstanding performance, detonation velocities ranging from 7141 to 10084 m/s, detonation pressures ranging from 25.10 to 58.04 GPa, and heat of detonation values from 1.11-1.91 kcal/g.

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A series of high-energy coordination polymers with 3,6-bis(4-nitroamino-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine, a ligand with multi- coordination sites, high oxygen content and detonation performance: Syntheses, structures, and performance

Cheng Shen,[a] Yuan-gang Xu[a] and Ming Lu*[a]

In this study, 3,6-Bis(4-nitroamino-1,2,5-oxadiazol-3-yl)-1,4,2,5-dioxadiazine (H_2BNOD), with a relatively high oxygen content (37.41%) and good detonation performance (density = 1.817 g/cm^3, detonation velocity = 8490 m/s), is used to prepare three new high-energy coordination polymers (CPs), $\{Ag_2(BNOD)(DMF)_2\}_n$ (1), $\{Ag_2(BNOD)\}_n$ (1a), $\{Cu(BNOD)(H_2O)_6\}_n$ (2), and a metal salt, $Co(BNOD)(H_2O)_6$ (3). Crystal structure analyses indicated that 1 exhibits 2D energetic coordination polymer (E-CP) with a three-dimensional wavy layer structure; (1a) exhibits compact 3D E-CP without any solvent molecules. 2 exhibits a zigzag 1D chain structure, while the ionic salt 3 is a layer-by-layer structure (0D). Thermal analysis indicated that 1 and 1a exhibit good, as well as similar, thermostability (200 °C) owing to their compact framework structures. The enthalpy of formation is calculated from constant-volume combustion energy. The four compounds exhibit detonation velocities (D) ranging from 7141 to 10084 m/s, detonation pressures (P) ranging from 25.10 to 58.04 GPa, and heat of detonation (Q) values from 1.11-1.91 kcal/g. The impact sensitivities of the energetic salts were between 5 and 12 J, and their friction sensitivities ranged from 120 to 180 N, at the same level with RDX and HMX. Among these four compounds, 1a exhibits outstanding performance (D = 10084 m/s, P = 58.04 GPa and Q = 1.91 kcal/g) with an compact 3D CP structure.

1 Introduction

Metal-based explosives have been designed as primary explosives (e.g., lead azide) because of their high sensitivity toward mechanical stimuli.[1] Currently, coordination polymers have been investigated in coordination chemistry and materials science. Because of their compact packing modes, inherent structural stability, high mechanical strength and intriguing architectures, energetic CPs have attracted considerable attention with the aim of further investigating their potential as new-generation explosives.[2] Abundant one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) E-CPs with remarkable energetic properties have been reported.[3] Results from these studies have revealed that E-CPs with a rigid structure exhibit high heat of detonation and high thermostability.

Previously, nitrogen-rich heterocycle-based energetic compounds have been explored and extensively reported as ligands, because of the advantages imparted by nitrogen-rich heterocycles, e.g., diverse coordination modes, abundant inherent energetic (N-N, 160 kJ mol^{-1}; N=N, 418 kJ mol^{-1}; N=-N, 954kJ mol^{-1}), and superior structural stability.[4] However, heterocycle-based energetic ligands, e.g., triazole and tetrazole derivatives, always exhibit bad oxygen-balance (OB) and low density, led to the relatively high carbon deposition and low detonation properties (in Fig. 1) (Atrz[2b], Hbta[5], H2tztr[6,]

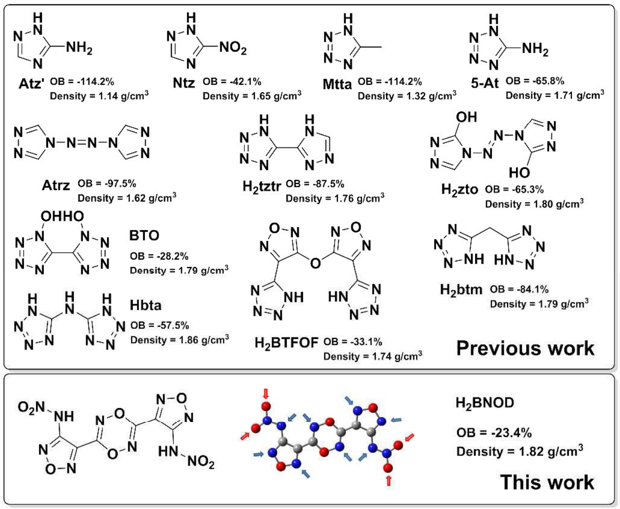

Fig. 1 Comparison between previous works and this work and the predict coordination sites of $BNOD^{2-}$

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[a] School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China. E-mail: luming@mail.njust.edu.cn; luming302@126.com

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[8], 5-At[7], atz[9], ntz[9], Mtta[10], H2BTFOF[11], BTO[12], H2btm[13], Hbta[14], H2zto[15]). Energetic groups such as -C-NO_2, -N-NO_2, and -ONO_2, can enhance the detonation performances, however, it is difficult to synthesize CPs for their strong electron-withdrawing effect[16], which have not enough electrons to coordinate with metal ions.

The latest research of our group has successfully synthesized two high-energy coordination polymers (HE-CPs) with a ligand (4,4'-bis(dinitromethyl)-3,3'-azofurazanate (H_2DNMAF)) containing high inherent energetic –C-NO_2 group and oxygen-rich furazan rings, which exhibit superior detonation performances.[17]

In this study, a novel energetic ligand with the furazan ring, dioxadiazine ring and high-energy-density nitroamino groups (H_2BNOD)[18] is used to successfully prepare new HE-CPs for its high oxygen content and good detonation performance. Such a structure is selected because of its diverse coordination and multi- coordination modes (more than 12 possible coordination sites in one ligand). In addition, H_2BNOD has been extensively investigated for high energy density materials for its high density, positive heat of formation, high oxygen content and detonation performance. As a ligand, it can be used as a valuable energetic unit for designing and constructing a unique class of energetic CPs and metal salts. In contrast, the good thermostability of CPs can also enhance the rather poor decomposition temperature of H_2BNOD (T_d=95 °C)[18b].

2 Experimental

2.1 Caution

Caution: Title compounds are dangerous materials, explosions of which may occur in certain conditions. Although we had no difficulties on synthesizing and handing the compounds, proper safety precautions such as safety glasses, plastic spatulas and face shields must be used, especially when the experiments on a large scale.

2.2 Materials and General Methods.

H_2BNOD was synthesized according to a previously reported method[18b]. Other commercially available reagents were used without further purification. The melting and decomposition (onset) points were measured on a differential scanning calorimeter (DSC, Mettler Toledo DSC823e) at a scan rate of 5 °C min^{-1} in closed Al containers with a nitrogen flow of 50 mL min^{-1}. In addition, thermogravimetric analysis (TGA) was carried out at a heating rate of 5 °C min^{-1} on a Mettler Toledo TGA/SDTA851e instrument. The infrared (IR) spectra of solids were recorded using KBr pellets on a Thermo Nicolet iS10 spectrometer. Elemental analyses were carried out on a Vario EL III CHNOS elemental analyzer.

2.3 Synthesis of compounds

Table 1 Crystal data and structure refinement for 1, 1a, 2, and 3

	1	1a	2	3
CCDC	1544456	1545528	1544367	1544457
Empirical formula	$C_6H_7AgN_6O_5$	$C_6Ag_2N_{10}O_8$	$C_6H_{12}CuN_{10}O_{14}$	$C_6H_{12}CoN_{10}O_{14}$
Formula weight	351.05	555.90	511.81	507.19
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P21/c	P21/n	P21/c	P21
a	10.7240(2)	8.6085(12)	5.1863(4)	8.1638(10)
b	8.2255(19)	8.3879(10)	16.5502(14)	12.1332(16)
c	12.527(3)	8.7084(12)	10.2480(9)	16.740(2)
α	90	90	90	90
β	103.154(5)	99.777(5)	93.952(4)	99.227(9)
γ	90	90	90	90
V	1076.0(4)	619.68(14)	877.54(13)	1636.7(4)
Z	4	2	2	4
D_c (g/cm^3)	2.167	2.979	1.937	2.058
T (K)	173	173	296	140
μ (mm^{-1})	1.901	3.242	1.346	1.158
F (000)	688.00	528.0	518.0	1028.00
GOF on F	1.032	1.049	1.093	1.026
R_1[I>2σ(I)]	0.0296	0.0399	0.0301	0.0518
wR_2(I>2σ(I))	0.0782	0.0566	0.0883	0.1211
R_1[all data]	0.0376	0.0724	0.0350	0.0768
wR_2(all data)	0.0805	0.0631	0.0909	0.1336

2.3.1 Synthesis of Ag_2(BNOD)·(DMF)$_2$ (1). First, an aqueous solution (1.5 mL) of $AgNO_3$ (0.266 mmol, 45.2 mg) was added to an aqueous solution (2 mL) of H_2BNOD (0.146 mmol, 50.0 mg) at room temperature. Second the resultant mixture was stirred for 5 min, filtered, and the filter cake was washed with water (5ml*3) to obtain off-white solid product. Next, the product was dissolved in 3 mL of DMF. The solution was added into a 5ml beaker. Then put the beaker into a 50ml beaker with water inside. Finally, by the diffusion of water vapor after 5 days, rhombic crystals suitable for X-ray diffraction (XRD) measurement were obtained. Yield: 55.4 mg (54%, based on H2BNOD). Elemental analysis (%) calcd for $Ag_2C_6N_{10}O_8\cdot 2(C_3H_7NO)$: C 20.53, H 2.01, N 23.94; found: C 20.63, H 2.52, N 23.78. IR (KBr, cm−1): 2931(w), 1644(s),1621(s), 1436(m), 1243(s), 1115(m), 1032(m), 873(m), 822(s).

2.3.2 Syntheses of Ag_2(BNOD) (1a). Solution A: $AgNO_3$ (0.266 mmol, 45.2 mg) was added in water (2.5 ml) and the mixture was stirred for 5 min. Solution B: $NaNO_3$ (0.212 mmol, 9 mg)

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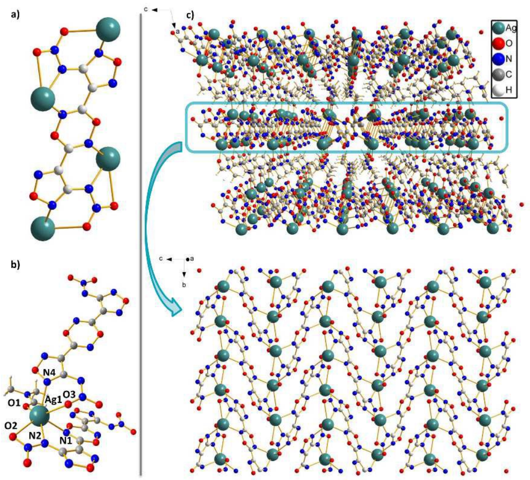

Fig. 2 Compound 1: (a) coordination environment of Ag(I) ion; (b) coordination model of the ligand; (c) The 3D network extended based on the chains and a top perspective view of the 2D layers.

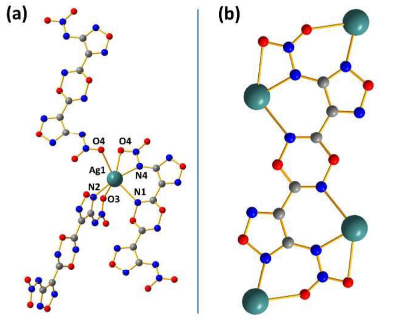

Fig. 4 (a) coordination environment of Ag(I) ion in 1a; (b) coordination model of the ligand of 1a

was added in water (1 ml). Solution C: H_2BNOD (0.146 mmol, 50.0 mg) in water (2.5 ml), which was ultrasound dissolved until clear. Solution A was placed into the bottom of a clean 1 centimeter diameter glass tube, and then B and C were slowly added, in turn, onto the surface of the previous solution, to form a diffusion system. By interfacial diffusion after 7 days, colorless rhombic crystals suitable for XRD measurement were obtained. Yield: 24.3 mg (30%, based on H_2BNOD). Elemental analysis (%) calcd for $Ag_2C_6N_{10}O_8$: C 12.96, H 0, N 25.20; found: C 13.02, H 0.02, N 25.12. IR (KBr, cm^{-1}): 1634(w), 1534(w), 1481(m), 1455(m), 1250(s), 1122(m), 1053(m), 840(m), 645(w).

2.3.3 Syntheses of Cu(BNOD)·6(H_2O) (2). First, an aqueous solution (1.5 mL) of $Cu(NO_3)_2$ (0.133 mmol, 24.9 mg) was added to an aqueous solution (2 mL) of H_2BNOD (0.20 mmol, 27 mg) at room temperature. Second, the resultant mixture was stirred for 5 min and filtered. The product solution was obtained as the filtrate. Next, the solution was volatilized at room temperature. Finally, blue rhombic crystals for XRD measurement were obtained after 5 days. Yield: 50.8 mg (68%, based on H_2BNOD). Elemental analysis (%) calcd for $CuC_6N_{10}O_8\cdot6(H_2O)$: C 14.08, H 2.36, N 27.37; found: C 14.04, H 2.30, N 27.45. IR(KBr, cm^{-1}): 3560(w), 3371(m), 3181(m), 1635(m), 1493(m), 1395(s), 1280(s), 1125(m), 1035(s), 691(m).

2.3.4 Syntheses of Co(BNOD)·6(H_2O) (3). Compound 3 was prepared by a procedure similar to that employed to prepare 2, except that $Cu(NO_3)_2$ was replaced by $Co(NO_3)_2$ (0.133 mmol, 24.3 mg). Yield: 19.2 mg (26%, based on H_2BNOD). Elemental analysis (%) calcd for $CoC_6N_{10}O_8\cdot6(H_2O)$: C 14.21, H 2.39, N 27.62; found: C 14.34, H 2.30, N 27.95. IR(KBr, cm^{-1}): 3420(m), 1639(m), 1499(m), 1274(s), 1132(m), 1013(m), 899(m), and 775(m).

2.4 Crystallographic Data Collection and Refinement

Singlecrystal X-ray experiments were performed on a Bruker Smart Apex II diffractometer using Mo-Kα radiation (λ = 0.71073 Å) with a graphite monochromator at 173 K, 173 K, 296K, and 140K. An Oxford Cobra low-temperature device was used to maintain low tempera-ture. The SAINT program[19] was employed for the integration and scaling of intensity data. The structures were solved by intrinsic phasing using SHELXT2014[20], and refinement was carried out by a full-matrix least-squares technique using SHELXT2014. The hydrogen atoms were refined isotropically, and the heavy atoms were anisotropically refined. The N-H and OH hydrogens were located from different electron density maps, and C-H hydrogens were placed at calculated positions and refinded with a riding model. Data were corrected for the absorption effects using SADABS[21] Table 1 summarizes the crystal data and refinement results.

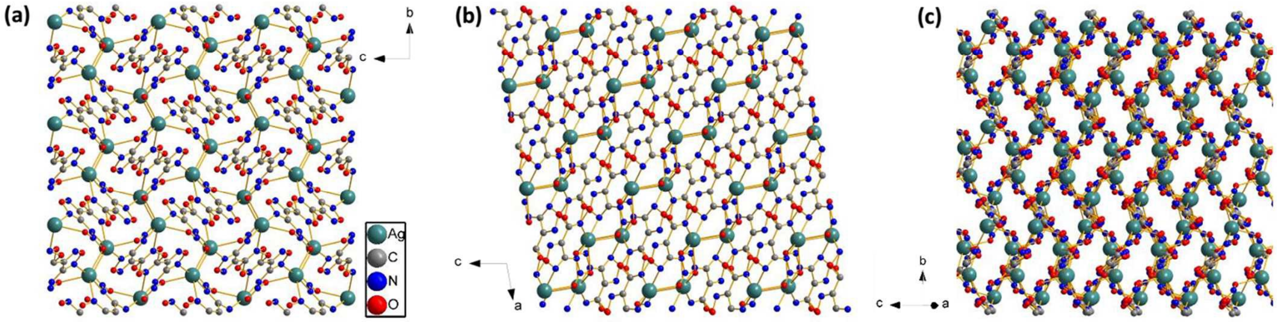

Fig. 3 (a) and (b) 3-D frameworks in 1a seen along the a- and b- axes respectively. (c) 3D porous structure of 1a.

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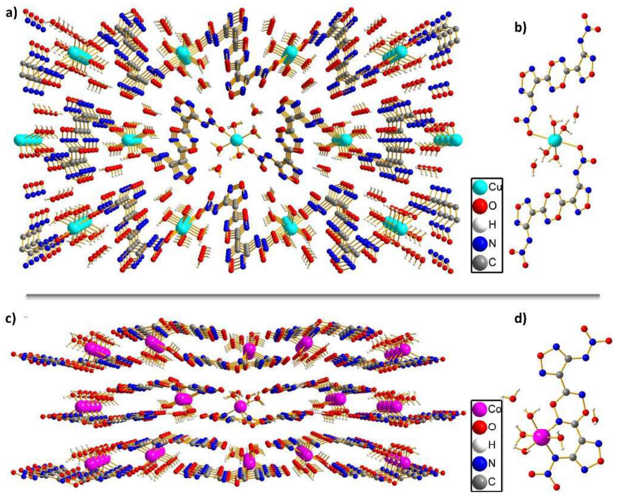

Fig. 5 (a) 1D chain structure in 2 along the a- axis; (b) coordination environment of Cu(II) ion in 2; (c) layer-by-layer structure in 3 along the a- axis; (d) coordination environment of Co(II) ion in 3.

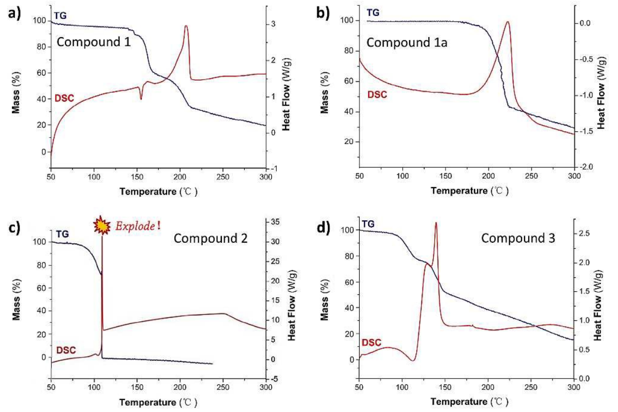

Fig. 6 (a), (b), (c), and (d) The TG-DSC curves of compound 1, 1a, 2, and 3, in order.

3 Results

3.1 Structural description

3.1.1 Crystal structure of 1. The single-crystal XRD analysis of 1 revealed that 1 crystallizes in the monoclinic space group P21/c with Z = 4. The asymmetric unit includes four crystallographically independent Ag(I) ions, two $BNOD^{2-}$ ligands, and two coordinated DMF molecules. The Ag(I) ion is hexa-coordinated to three nitrogen atoms from two $BNOD^{2-}$ ligands [Ag1-N1 = 2.567(3) Å, Ag1-N2 = 2.265(3) Å, and Ag1-N4 = 2.504(3) Å], three oxygen atoms from $BNOD^{2-}$ [Ag1-O2 = 2.824 (3), Ag1-O3 = 2.774(2) Å] and DMF molecules [Ag1-O1 = 2.277(2) Å] (Fig. 2b). In this way, each $BNOD^{2-}$ functions as a decadentate ligand bridging four Ag(I) ions, forming a 2D framework (wavy layers) along the b-axis, the gaps of this 2D framework are filled with coordinated DMF molecules (Fig. 1c). The single layer was investigated further. Interestingly, each Ag(I) cation form two six-membered rings with two $BNOD^{2-}$ ligands (Fig. 1a), generating 2D network structures (Fig. 1c)

3.1.2 Crystal structure of 1a. The single-crystal XRD analysis of 1a revealed that 1a crystallizes in the monoclinic space group P21/n with Z = 2. The asymmetric unit includes two crystallographically independent Ag(I) ions and one $BNOD^{2-}$ ligand. The Ag(I) ion is hexa-coordinated to three nitrogen atoms from the six-membered ring of $BNOD^{2-}$ [Ag1-N1 = 2.618(5) Å, Ag1-N2 = 2.252(5) Å, Ag1-N4 = 2.251(5) Å] and three oxygen atoms from the nitro groups of $BNOD^{2-}$ [Ag1-O3 = 2.582(4), Ag1-O4 = 2.680(4) Å, Ag1-O4 = 2.784(4) Å] (Fig. 4a). In this way, each BNOD2- also functions as a decadentate ligand bridging four Ag(I) ions, forming a 3D framework. Furthermore, each Ag(I) cation form two six-membered rings with two $BNOD^{2-}$ ligands (Fig.4b), which is the same as 1 in Fig. 1a, generating 3D network structures (Fig. 3)

3.1.3 Crystal structure of 2. From the XRD crystallography data, 2 crystallizes in the monoclinic space group P21/c with Z = 2 as a zigzag mononuclear 1D chain structure. The asymmetric unit is crystallographically independent with two Cu(II) ions, two $BNOD^{2-}$ ligands, and 12 coordination water molecules. As shown in Fig.5b, the Cu(II) ion is hexa-coordinated to two oxygen atoms ($-NO_2$) from two $BNOD^{2-}$ ligands and four oxygen atoms from water molecules in a stretched octahedral shape. The Cu-O bond lengths range from 1.927(2) to 1.978(2) Å. The O-Cu-O bond angle is 180.000° (Fig. 5a and 5b).

3.1.4 Crystal structure of 3. Compound 3 crystallizes in the monoclinic space group, P21, Z = 4, as a layer-by-layer structure. The asymmetric unit is crystallographically independent with four Co(II) ions, four $BNOD^{2-}$ ligands, and 24 coordination water molecules. The Co(II) cation is hexa-coordinated to two nitrogen atoms and four oxygen atoms, generating a slightly distorted octahedron (Fig. 5d). The structure is closely connected by H-bonds, affording a layer-by-layer supramolecular network (Fig.5c). The dianionic ligand $BNOD^{2-}$ binds to the Co(II) ion as a metal salt, affording an intra-ion six-membered ring. The Co-O bond lengths range from 2.070(6) to 2.095(6) Å. Two Co-N bond lengths are 2.148(6) Å and 2.150(7) Å. The N-Co-N bond angle is 84.265(251) °

3.2 Thermal decomposition

Simultaneous TGA -DSC measurements were carried out at a linear heating rate of 5 °C min^{-1} under nitrogen to evaluate the thermal stabilities of 1, 1a, 2, and 3. Fig. 6 shows the result. Compound 1 $\{Ag_2(BNOD)(DMF)_2\}_n$, and 1a $\{Ag_2(BNOD)\}_n$ have the similar element composition (1 has two additional coordinated DMF molecules compared to 1a). The TGA-DSC curve revealed that the thermal decomposition of 1 begins at 200.05 °C and ends at 221.40 °C with a peak temperature at 206.99 °C. Another mass loss with endothermic peaks is observed at 154.88 °C, corresponding to the loss of two coordinated DMF molecules. The curve of 1a revealed that exothermic decomposition occurs between 199.39°C and 230.24°C, with a peak temperature of 221.51°C. No mass loss corresponding to DMF or H_2O molecules is observed for 1a.

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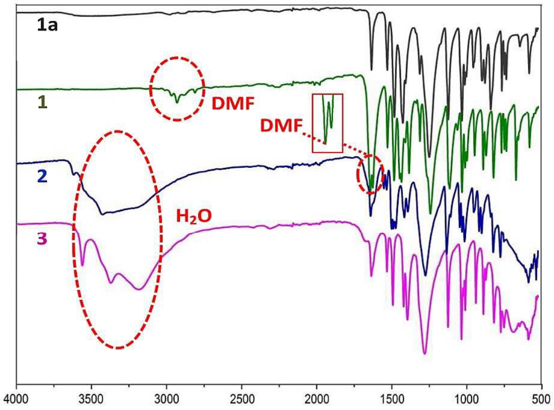

Fig. 7 The IR spectrums of 1, 1a, 2, and 3

In the TGA-DSC curve of 2 $\{Cu(BNOD)(H_2O)_6\}_n$, a strong explosion occurs at 108.40 °C. The main intense exothermic process of 3 $Co(BNOD)(H_2O)_6$ ranges from 129.68 °C to 150.13°C, with a peak temperature of 136.72°C. The mass loss at around 100 °C corresponds to the loss of coordinated H_2O molecules.

3.3 Vibrational spectroscopy

As shown in the IR spectra (Fig.7), peaks for 1 are observed at 2931 cm^{-1} (C-H stretch and shear vibrations) and 1644 cm^{-1} (N-C=O asymmetric stretch) corresponding to the DMF ligands. The curves of 1 and 1a are compared, except the above two peaks belonging to DMF, and considerably similar IR spectra are observed. 1a and 1 share the same ligand and central metal atom, while 1a has no DMF ligands. Moreover, for 2 and 3, the vibration of water peaks is clearly observed at 3000-3600 cm^{-1}.Hence, the structure of 1a does not contain water molecules.

3.4 Oxygen-bomb calorimetry and enthalpy of formation

The constant-volume combustion energies ($\Delta_c U$) of 1-3 were measured using a rotating-oxygen bomb calorimeter (Parr 6400, Parr Instrument Company, Moline Illinois, USA). Approximately 50 mg of the sample was pressed with a well-define amount of benzoic acid (calcd 250 mg, NIST Thermochemical Standard 39j) to form a tablet, which ensures better combustion. The standardization test is the same as that employed for the E-MOF sample. The recorded data represent an average of five single measurements.

From the experimental, the $\Delta_c U$ values for 1, 1a, 2, and 3 are -11023.1 J/g, -8068.2 J/g, -7259.9 J/g, and -7136.4 J/g, respectively. According to $\Delta_c H_m^\theta = \Delta_c U + \Delta nRT$, $\Delta \mathrm{n} = \mathrm{n}_g(products) - \mathrm{n}_g(reactants)$, (where n_g is the total molar amount of gases in the products or reactants, R = 8.314 Jmol-1K-1 and T=298.15 K)[22], the enthalpies of combustion $\Delta_c H_m^\theta$ are calculated as -7721.5kJ/mol, -4468.7 kJ/mol, -4049.0 kJ/mol, and -4656.2 kJ/mol, in order as the ideal combustion reaction (1)-(4).

$$Ag_2C_{12}H_{14}N_{12}O_{10}(s) + 11O_2(g) = Ag_2O(s) + 7H_2O(l) + 12CO_2(g) + 6N_2(g) \quad (1)$$

$$Ag_2C_6N_{10}O_8(s) + \frac{5}{2}O_2(g) = Ag_2O(s) + 6CO_2(g) + 6N_2(g) \quad (2)$$

$$CuC_6H_{12}N_{10}O_{14}(s) + \frac{5}{2}O_2(g) = CuO(s) + 6H_2O(l) + 6CO_2(g) + 5N_2(g) \quad (3)$$

$$CoC_6H_{12}N_{10}O_{14}(s) + \frac{5}{2}O_2(g) = CoO(s) + 6H_2O(l) + 6CO_2(g) + 5N_2(g) \quad (4)$$

The standard molar enthalpy of formation ($\Delta_f H_m^\theta$) values for 1, 1a, 2, and 3 are calculated by Hess's law[23] as 967.57 kJ/mol, 2863.7 kJ/mol, -184.4 kJ/mol, and 342.2 kJ/mol, respectively.

3.5 Detonation properties

Detonation velocity (D), detonation pressure (P) and heat of

Table 2 Detonation properties of compounds 1, 1a, 2 and 3

Compound	Density (g/cm^3)	T_d (℃)[a]	OB (CO_2) (%)	Q (kcal/g)	P (GPa)	D (m/s)	IS (J)[b]	FS (N)[c]
1	2.167	200.05	-50.1	1.11^d	24.10^d	7141^d	12	180
1a	2.979	199.39	-14.4	1.91^d	58.04^d	10084^d	7.5	120
2	1.937	108.40	-17.2	1.21^d	28.99^d	7913^d	5	120
3	2.058	129.58	-15.8	1.23^d	28.19^d	7672^d	7.4	120
TNT[26]	1.654	244	-74.0	$1.44^d/1.22^e$	$21.95^d/20.50^e$	$7220^d/7178^e$	15	353
HMX[26]	1.910	287	-21.6	$1.62^d/1.32^e$	$40.36^d/38.39^e$	$9374^d/8900^e$	7.4	-
RDX[26]	1.806	210	-21.6	$1.59^d/1.44^e$	$35.77^d/33.92^e$	$8971^d/8600^e$	7.5	120
$[Cu(tztr)]_n$[27]	2.216	360	-52.3	$2.78^d/3.40^e$	$31.15^d/40.02^e$	$7909^d/8429^e$	>40	>360
$\{[Cu(tztr)]\ H_2O\ \}$[8]	2.316	80/325	-48.0	$1.32^d/1.32^e$	$26.80^d/31.99^e$	$7254^d/7920^e$	>40	>360
$[Cu(artz)_3(NO_2)_2]_n$[2b]	1.68	243	-58.8	$3.62^d/3.62^e$	$34.44^d/35.68^e$	$9000^d/9126^e$	22	5
$[Ag(artz)_{1.5}(NO_2)]_n$[2b]	2.16	257	-50.0	$1.38^d/1.38^e$	$30.80^d/29.70^e$	$7918^d/7773^e$	30	-
ZnHHP[28]	2.117	293	-50.0	0.7^e	23.58^e	7016^e	-	-
$[Pb(Htztr)_2(H_2O)]_n$[6]	2.519	214/340	-45.0	$1.73^d/1.36^e$	$20.11^d/31.57^e$	$6432^d/7715^e$	>40	>360
$[Cu(ntz)]_n$[29]	2.428	315	-22.6	$1.82^d/1.47^e$	$31.07^d/33.10^e$	$7721^d/7970^e$	>40	>360
$[Cu(ntz)(N_3)(DMF)]_n$[29]	1.801	199/279	-60.3	$1.99^d/1.81^e$	$23.29^d/16.04^e$	$7245^d/6080^e$	>40	>360
$[Cu(ntz)(N_3)(H_2O)]_n$[29]	2.218	109/287	-16.9	$0.09^d/0.02^e$	$7.75^d/4.46^e$	$3943^d/2220^e$	>40	>360

[a] Decomposition temperature. [b] Impact sensitivity. [c] Friction sensitivity. [d] calculation method in this work. [e] literature values

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detonation (Q) are the most important parameters that evaluate the performance of explosives. On the basis of the Becker–Kistiakowsky–Wilson's (BKW) equation[24] and the Kamlet- Jacobs (K-J) method[22], a simple method has been reported by Pang and coworkers for calculating the detonation performance of metal-containing explosives. This method has been used to calculate metal salts and E-CPs in many literatures published worldwide.[10,12,17,25] In this study, the method is employed to calculate the detonation parameters. Furthermore, OB is another important parameter for energetic materials, which determines if the compounds are enriched or poor in oxygen.

$$Ag_2C_{12}H_{14}N_{12}O_{10} = 2Ag + 10.5C + 7H_2O + 1.5CO_2 + 6N_2 \quad (5)$$

$$Ag_2C_6N_{10}O_8 = 2Ag + 2C + 4CO_2 + 6N_2 \quad (6)$$

$$CuC_6H_{12}N_{10}O_{14} = Cu + 2C + 6H_2O + 4CO_2 + 5N_2 \quad (7)$$

$$CoC_6H_{12}N_{10}O_{14} = Co + 2C + 6H_2O + 4CO_2 + 5N_2 \quad (8)$$

$$\mathrm{D} = 1.01\left(N\bar{M}^{1/2}Q^{1/2}\right)(1 + 1.30\rho) \quad (9)$$

$$\mathrm{P} = 1.55\rho^2\mathrm{N}\bar{\mathrm{M}}^{1/2}\mathrm{Q}^{1/2} \quad (10)$$

$$\mathrm{Q} = \frac{-[\Delta H_f(detonation\ products) - \Delta H_f(explosive)]}{Mw} \quad (11)$$

Where D is the detonation velocity, P is the detonation pressure, Q is heat of detonation, N is the number of moles of the gas generated per gram, $\bar{\mathrm{M}}$ is the average molecular weight of the gaseous product, and ρ is the crystal density.

According to the above methods, Q, D, P, and OB (CO_2) are calculated. Mechanical sensitivities are also measured. Table 2 summarizes the values of these parameters.

As shown in Table 2, 1a exhibits outstanding Q (1.91 kJ/g), D (10084 m/s) and P (58.04 GPa) values, while its mechanical sensitivity is still the same level as that of RDX. Such superior performance is related to the compact CP structure and the favorable properties, i.e., a multidentate solvent-free structure, OB, high density, and outstanding detonation properties of the good ligand (H_2BNOD). In addition, 1, 2, and 3 exhibit rather good detonation properties: D (7141 m/s, 7913 m/s, and 7672 m/s, respectively), Q (1.11kJ/g, 1.21 kJ/g, and 1.23 kJ/g, respectively) and appropriate stability (IS 5-12 J, FS 120-180 N). On the other hand, the CP structure enhances the thermostability from 95 °C to 200 °C. Furthermore, the T_d of 1 and 1a are much higher than 2 and 3. This may be caused by different coordination modes with different metal atoms. The BNOD2- in 1 and 1a functions as a decadentate ligand bridging Ag(I) ions, forming compact frameworks, and each Ag(I) cation form two six-membered rings with ligand, while BNOD^{2-} is only a bidentate ligand in 2 and 3 to from a zigzag mononuclear 1D chain or a layer-by-layer structure. The multi coordination sites can not only raise the crystal density but also enhance the stability of the structures.

4 Discussions

In this study, the new screened ligand with nitro groups contains greater than 10 coordination sites. Owing to the multidentate structure of the ligand, four new crystal compounds (1, 1a, 2, and 3) with three coordination modes are synthesized. Furthermore, 1 exhibits a special 3D wavy layer-by-layer structure, and 1a exhibits an compact 3D coordination polymer structure, which all leads to remarkably enhanced thermostability (from 95 °C to 200 °C); in addition 1a exhibits excellent detonation properties: D is 10084 m/s, Q is 1.91 kJ/g, and P is 58.04 GPa, which is even at a same level with CL-20[33]. These superior explosive behaviors can be formed as several reasons below.

In Fig. 8, based on the crystal data, a 2*2*2 cell of 1a has been created and the density is 2.979 g/cm^3. Then we remove all silver atoms in this cell and the density turns to be 1.823 g/cm^3, which can be regard as the partial density for the ligand BNOD^{2-}. The value (1.823 g/cm^3) is even higher than the literature crystal density of H_2BNOD (1.817 g/cm^3)[24]. Although the sliver atom has a rather large atomic radius, the partial density of ligand is still not less than the literature crystal density of H_2BNOD. This comparison study can prove that the introduction of sliver can make the structure more compact. Even though the higher density (2.979 g cm^{-3}) is partially caused by dinuclear silver ions, the compact structure also keeps the partial density of ligand at a good level.

Moreover, one multidentate structure of the ligand in 1a forms ten coordination bonds with sliver atoms. Different from low-energy ionic bonds, the coordination bond length is

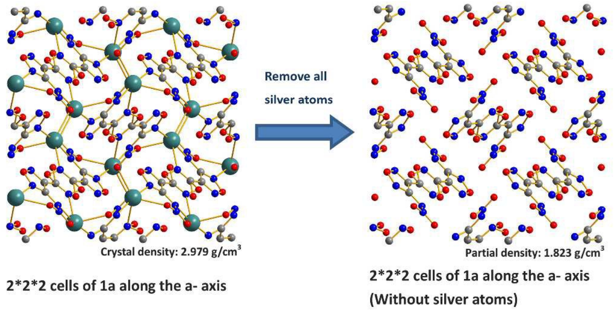

Fig. 8 Crystal density and partial density of ligand for 1a in 2*2*2 cells.

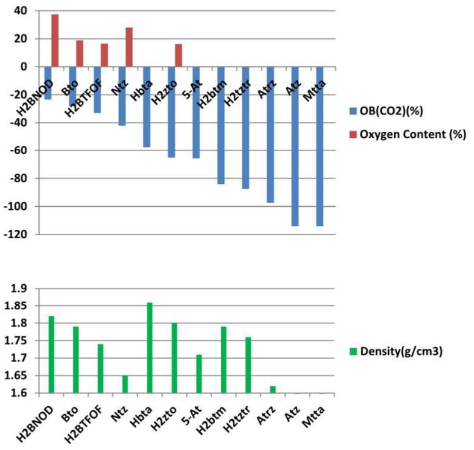

Fig. 9 Density, oxygen balance and oxygen content of ligands in the literature and in this paper.

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shorter and the coordination bond energy is higher.

In conclusion, the select ligand (H_2BNOD) with good properties (density = 1.817 g/cm^3 and D = 8490 m/s) leads to plentiful coordination bonds (high energy) and a compact CP structure (high density). Moreover, H_2BNOD exhibits the best OB as well as better density compared to previously reported ligands of E-CPs (Fig. 9).

5 Conclusions

In conclusion, a new screened ligand, 3,6-bis(4-nitroamino-1,2,5-oxadiazol-3-yl)-1,4,2,5- dioxadiazine dianion, with an oxygen-rich furazan ring, high density nitroamino groups and good detonation performance, used to synthesize novel HE-CPs. A 2D Ag-CP 1, a 3D Ag-CP 1a, a 1D copper CP 2, and a cobalt energetic salt 3 are synthesized. Compounds 1–3 are characterized by single crystal X-ray diffraction, elemental analysis, IR spectroscopy, and TGA-DSC analyses. Crystal structure analyses revealed that 1 comprises 2D E-CP with a 3D wavy layer-by-layer structure, compound 1a exhibits a compact 3D structure, 2 exhibits a zigzag 1D chain structure, and 3 exhibits a layer-by-layer structure. The experimental results revealed that 1 and 1a exhibit excellent thermal stability up to 200 °C.

Compared with the E-CPs reported previously, 1a exhibits an outstanding values for D (10084 m/s), P (58.04 GPa) and Q (1.91 kcal/g) and 1 exhibits relatively poor D and P, where the coordinated solvent DMF molecule weakens the values of D and P. This study confirmed that new screened ligand H_2BNOD plays an important role in the enhancement of detonation performance. The -N-NO_2 group can serve as the coordination site to prepare E-CPs. Further research on better energetic CPs is underway.

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References

1 (a) Y. Tang, C. He, L. A. Mitchell, D. A. Parrish, and J. M. Shreeve, Angew. Chem. Int. Ed., 2016, 128, 5655-5657; (b) T. M. Klapötke, N. Mehta, Propellants Explos. Pyrotech., 2014, 39, 7-8.

2 (a) X. Liu, X. Qu, S. Zhang, H. Ke, Q. Yang, Q. Shi, Q. Wei, G. Xie, and S. Chen, Inorg. Chem. 2015, 54, 11520-11525; (b) S. Li, Y. Wang, C. Qi, X. Zhao, J. Zhang, S. Zhang, and S. Pang, Angew. Chem. Int. Ed., 2013, 52, 14031-14035; (c) J. Zhang, Y. Du, K. Dong, H. Su, S. Zhang, S. Li, and S. Chen, Chem. Mater., 2016, 28, 1472-1480.

3 (a) Q. Zhang and J. M.Shreeve, Angew. Chem. Int. Ed. 2014, 53, 2540-2542; (b) J. Zhang and J. M.Shreeve, Dalton Trans., 2016, 45, 2363-2368.

4 (a) R. P. Singh, R. D. Verma, D. T. Meshri, and J. M. Shreeve, Angew. Chem., Int. Ed., 2006, 45, 3584-3601; (b) M. Friedrich, J. C. Gálvez-Ruiz, T. M. Klapötke, P. Mayer, B. Weber, and J. J. Weigand, Inorg. Chem., 2005, 44, 8044-8052.

5 S. Zhang, X. Liu, Q. Yang, Z. Su, W. Gao, Q. Wei, G. Xie, S. Chen, and S. Gao, Chem. Eur. J., 2014, 20, 7906-7910.

6 W. Gao, X. Liu, Z. Su, S. Zhang, Q. Yang, Q. Wei, S. Chen, G. Xie, X. Yanga, and S. Gao, J. Mater. Chem. A, 2014, 2, 11958-11965.

7 Q. Zhang, D. Chen, X. He, S. Huang, J. Huang, X. Zhou, Z. Yang, J. Li, H. Li and F. Nie, CrystEngComm, 2014, 16, 10485-10491.

8 X. Liu, W. Gao, P. Sun, Z. Su, S. Chen, Q. Wei, G. Xie, and S. Gao, Green Chem., 2015, 17, 831-836.

9 X. Qu, S. Zhang, Q. Yan, Z. Su, Q. Wei, G. Xie and S. Chen, New J. Chem., 2015, 39, 7849-7857.

10 K. A. McDonald, S. Seth, and A. J. Matzger, Cryst. Growth Des., 2015, 15, 5963-5972.

11 X. Qu, S. Zhang, B. Wang, Q. Yang, J. Han, Q. Wei, G. Xie, and S. Chen, Dalton Trans., 2016, 45, 6968-6973.

12 Y. Shang, B. Jin, R. Peng, Q. Liu, B. Tan, Z. Guo, J. Zhao, and Q. Zhang, Dalton Trans., 2016, 45, 13881-13887.

13 Y. Feng, Y. Bi, W. Zhao, and T. Zhang, J. Mater. Chem. A, 2016, 4, 7596-7600.

14 Q. Liu, B. Jin, Q. Zhang, Y. Shang, Z. Guo, B. Tan, and R. Peng, Materials 2016, 9, 681-695.

15 X. Song, S. Zhang, G. Zhao, W. Zhang, D. Chen, Q. Yang, Q. Wei, G. Xie, D. Yang, S. Chen, and S. Gao, RSC Adv., 2016, 6, 93231-93237.

16 C. Bian, K. Wang, L. Liang, M. Zhang, C. Li, and Z. Zhou, Eur. J. Inorg. Chem., 2014, 35, 6022-6030.

17 C. Shen, Y. Liu, Z. Zhu, Y. Xu, and M. Lu, Chem. Comm., 2017, 53, 7489-7492.

18 (a) H. Huang, Y. Shi, Y. Liu, and J. Yang, Dalton Trans., 2016, 45, 15382-15389; (b) S. D. Shaposhnikov, T. V. Romanova, N. P. Spiridonova, S. F. Mel'nikova, and I. V. Tselinskii, Russ. J. Org. Chem., 2004, 40, 884-888.

19 SAINT v7.68A Bruker AXS inc.:Madison, WI (2009).

20 G. M. Sheldrick, SHELXL-2014/7, University of Gottingen, Germany (2014).

21 SADABS v2008/1 Bruker AXS Inc.: Madison, WI (2008).

22 (a) K. M. J. and S. T. Jacobs, J. Chem. Phys., 1968, 48, 23-35; (b) J. D. Cox, D. D. Wagman, and V. A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere Publishing Corp, New York, 1989.

23 P. W. Atkins, Physical Chemistry, Oxford University Press, Oxford, 1982.

24 (a) Y. Wang, J. Zhang, H. Su, S. Li, S. Zhang, and S. Pang, J. Phys. Chem. A, 2014, 118(25), 4575-4581; (b) A. Bondi, J. Phys. Chem., 1964, 68 (3), 441-451.

25 (a) Y. Xu, W. Liu, D. Li, H. Chen and M. Lu, Dalton Trans., 2017, DOI: 10.1039/C7DT02582C; (b) J. Zhang, Y. Du, K. Dong, H. Su, S. Zhang, S. Li, S. Pang, Chem. Mater., 2016, 28, 1472-1480; (c) Z. Guo, W. Wu, C. Deng, G. Yang, J. Zhang, Z. Sun, H. Ma, and C. Gao, An, Zhongwei, Inorg. Chem., 2016, 55, 11064-11071; (d) H. Zhang, M. Zhang, P. Lin, V. Malgras, J. Tang, S. M. Alshehri, Y. Yamauchi, S. Du, J. Zhang, Chem. Eur. J., 2016, 22,1141-1145; (e) Q. Yang, X. Song, W. Zhang, L. Hou, Q. Gong, G. Xie, Q. Wei, S. Chen, and S. Gao, Dalton Trans., 2017, 46, 2626-2634; (f) Q. Yang, G. Yang, W. Zhang, S. Zhang, Z. Yang, G. Xie, Q. Wei, S. Chen, S. Gao, Chem. Eur. J., 2017, 23, 9149-9155; (g) W. Fu, B. Zhao, M. Zhang, C. Li, H. Gao, J. Zhang, Z. Zhou, J. Mater. Chem. A, 2017, 5, 5044-5054; (h) Q. Yang, X. Song, G. Zhao, G. Yang, L. Yang, Q. Wei,

View Article Online
DOI: 10.1039/C7TA05479C

G. Xie, S. Chen, and S. Gao, Eur. J. Inorg. Chem., 2016, 31, 5052-5056; (i) M. Zhang, W. Fu, C. Li, H. Gao, L. Tang, Z. Zhou, Eur. J. Inorg. Chem., 2017, 22, 2883-2891; (j) Y. Feng, H. Qiu, S. Yang, J. Du, T. Zhang, Dalton Trans., 2016, 45, 17117-17122.

26 C. Shen, P. Wang, and M. Lu, J. Phys. Chem. A, 2015, 119 (29), 8250-8255.

27 Y. Zhang, S. Zhang, L. Sun, Q. Yang, J. Han, Q. Wei, G. Xie, S. Chen, and S. Gao, Chem. Commun., 2017, 53, 3034-3037.

28 O. S. Bushuyev, G. R. Peterson, P. Brown, A. Maiti, R. H. Gee, B. L. Weeks, and L. J. Hope-Weeks, Chem. Eur. J., 2013, 19, 1706-1711.

29 X. Qu, L. Zhai, B. Wang, Q. Wei, G. Xie, S. Chen, and S. Gao, Dalton Trans., 2016, 45, 17304-17311.