

# Preparation, crystal structures, thermal decompositions and explosive properties of two new high-nitrogen azide ethylenediamine energetic compounds†

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Two new multi-ligand coordination compounds of copper(II) ethylenediamine (en) azide and cobalt(III) ethylenediamine azide,  $[\text{Cu}_2(\text{en})_2(\text{N}_3)_4]_n$  (**1**) and  $\text{Co}(\text{en})_2(\text{N}_3)_2(\text{NO}_3)$  (**2**), were synthesized and characterized by elemental analysis and FT-IR spectroscopy. The crystal structures were determined by X-ray single crystal diffraction. The obtained results show that the crystals of **1** and **2** belong to the *monoclinic*, *C2/c* space group. The metal cations are six-coordinated with the azido ligands and ethylenediamine molecules through nitrogen atoms. The coordination modes of the azido-groups were  $\mu$ -1,  $\mu$ -1,1 and  $\mu$ -1,1,3 modes for **1**, and  $\mu$ -1 mode for **2**. Under a nitrogen atmosphere, with a heating rate of  $5 \text{ K min}^{-1}$ , the thermal decompositions contain two main exothermic stages in the DSC curves corresponding to the TG-DTG curves. The non-isothermal kinetics parameters were calculated by the Kissinger's method and Ozawa's method, respectively. The energies of combustion, enthalpies of formation, critical temperature of thermal explosion, entropies of activation ( $\Delta S^\ddagger$ ), enthalpies of activation ( $\Delta H^\ddagger$ ), and free energies of activation ( $\Delta G^\ddagger$ ) were measured and calculated. The sensitivity properties were also determined with standard methods and the results showed that **1** had a much higher flame sensitivity and lower impact sensitivity.

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## Introduction

Green energetic materials encompassing all propellants, explosives and pyrotechnics have long attracted intense research interest in the chemical sciences, with participating scientists including Klapötke,<sup>1–8</sup> Shreeve,<sup>9–13</sup> and so on.<sup>14,15</sup> It has become imperative to develop novel high-energy-density-materials (HEDM) which have good thermal stability, mechanical insensitivity and better performances, while being economic and having environmentally-friendly synthesis processes, in order to meet the requirements of future civil and military applications.<sup>16</sup>

Azido anions ( $\text{N}_3^-$ ) are widely used as bridging groups in the reported compounds because of their effective exchange interactions with versatile coordination modes (Fig. 1), which enables the construction of compounds with great diversity depending on the reaction environment. An azido ion can bind

to the metal *via* the  $\mu$ -1 mode (as a monodentate bridging ligand), the  $\mu$ -1,3 and  $\mu$ -1,1 modes (as a bidentate ligand), or the  $\mu$ -1,1,1 and  $\mu$ -1,1,3 modes (as a tridentate ligand). In addition, the nitrogen-rich azide compounds have a high heat of formation because they can release enormous amounts of energy, which is due to the average bond energies:  $\text{N-N}$  ( $160 \text{ kJ mol}^{-1}$ ),  $\text{N=N}$  ( $418 \text{ kJ mol}^{-1}$ ) and  $\text{N}\equiv\text{N}$  ( $954 \text{ kJ mol}^{-1}$ ). Recently, many scientists have researched energetic azide salts and compounds.<sup>4,9,17–19</sup> Ma *et al.*<sup>20</sup> synthesized and structurally characterized the azide compound of  $[\text{Mn}_3(\text{N}_3)_6(\text{admtrz})_4]_n$  (admtrz = 4-amino-3,5-dimethyl-1,2,4-triazole). The azido-group has three different coordination modes:  $\mu$ -1,  $\mu$ -1,3 and  $\mu$ -1,1. Bose *et al.*<sup>21</sup> reported the synthetic details, characterization data and single crystal X-ray structural analyses of  $[\text{Zn}(\text{dpa})(\text{N}_3)_2]$  and  $[\text{Zn}(\text{dpa})(\text{N}_3)(\text{NO}_3)]_2$  (dpa = 2,2'-dipyridylamine), and the azido-groups coordination modes were  $\mu$ -1 and  $\mu$ -1,1, respectively. Zhu *et al.*<sup>22</sup> reported the nickel(II) hydrazine azide, which is a potentially powerful primary explosive. Sheng *et al.*<sup>23</sup> also reported tetraamminediazido cobalt(III) perchlorate (DACP), which was very sensitive to a laser wavelength of 635 nm. We have studied the crystal structures, thermal decomposition mechanisms and sensitivity properties of  $\text{Cu}(\text{IMI})_4(\text{N}_3)_2$

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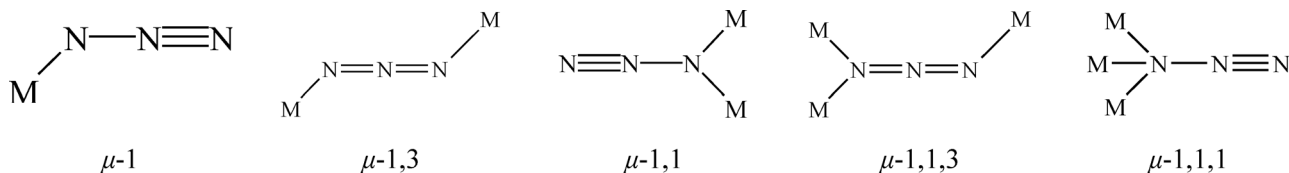


Fig. 1 Different coordination modes of the azido ligand.

Table 1 Straight-chain energetic ligands and their nitrogen contents

Chemical names	Nitrogen	Hydrazine (HZ)	Ammonia	Carbohydrazide (CHZ)	Ethylenediamine (en)	Methylamine
Chemical formulas	N <sub>2</sub>	H <sub>2</sub> NNH <sub>2</sub>	NH <sub>3</sub>	H <sub>2</sub> NNHCONHNH <sub>2</sub>	H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	H <sub>2</sub> NCH <sub>3</sub>
Nitrogen content (%)	100	87.42	82.24	62.19	46.61	45.10

and Ni(IMI)<sub>4</sub>(N<sub>3</sub>)<sub>2</sub> (IMI = Imidazole), and the azido-groups have only one  $\mu$ -1 coordination mode.<sup>18</sup> So the azido compounds have a potential application as energetic materials.

Ethylenediamine (en) has a strong coordination capacity as a bidentate ligand.<sup>19,24–41</sup> In the straight-chain energetic ligands (Table 1), en has a 46.61% nitrogen content. Ma *et al.*<sup>30</sup> reported the crystal structure of [Cd(en)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](MO)<sub>2</sub> [MO = (CH<sub>3</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>N = NC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na]. It displays a two-dimensional supramolecular layer structure and the en ligand acts as a bidentate ligand. In our research group, we have studied the synthesis, thermal decomposition and explosive properties of the energetic compounds [Cd(en)(N<sub>3</sub>)<sub>2</sub>]<sub>n</sub>,<sup>19</sup> [Cu(en)<sub>2</sub>(NF)<sub>2</sub>] and [Cd(en)<sub>3</sub>](NF)<sub>2</sub> (NF = nitroformate),<sup>42</sup> where the en ligand acts as a bidentate ligand, forming with the central metals. For the hydrazine (HZ) and carbohydrazide (CHZ) ligands, we have studied the synthesis, thermal decomposition and explosive properties of energetic compounds [Cd<sub>2</sub>(HZ)<sub>2</sub>(N<sub>3</sub>)<sub>4</sub>]<sub>n</sub>,<sup>43</sup> [Zn(HZ)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]<sub>n</sub><sup>17</sup> and Mn(CHZ)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>,<sup>44</sup> and found that they have good impact sensitivity. Furthermore, in the [Cd<sub>2</sub>(HZ)<sub>2</sub>(N<sub>3</sub>)<sub>4</sub>]<sub>n</sub> compound, the Cd(1) cations are coordinated by one azido group acting as a  $\mu$ -1 bridge, one azido group acting as a  $\mu$ -1,3 bridge, and two azido groups acting as  $\mu$ -1,1 bridges. The Cd(2) atoms are coordinated in a distorted octahedral environment by azido groups acting as  $\mu$ -1,3 and  $\mu$ -1 bridging ligands. In the [Zn(HZ)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]<sub>n</sub> compound, the central zinc(II) cations are coordinated by two azido groups acting as  $\mu$ -1 bridging ligands and four N atoms of the bidentate hydrazine ligands. In the Mn(CHZ)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub> compound, the azido-group has only one  $\mu$ -1 coordination mode.

In order to deepen the studies on the metal azide compounds, two new multi-ligand coordination compounds of [Cu<sub>2</sub>(en)<sub>2</sub>(N<sub>3</sub>)<sub>4</sub>]<sub>n</sub> (1) and Co(en)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>(NO<sub>3</sub>) (2) were synthesized and their crystal structures, the thermal decomposition mechanisms and sensitivity properties were studied in the present work.

## Results and discussion

### Molecule structures

The perspective views of the compounds are shown in Fig. 2 and the selected bond distances and angles of the title compounds are listed in Table 2 and 3.

In 1, there is one Cu(II) cation, four azido ligands and one ethylenediamine molecule that acts as a bidentate bridging ligand, however, there are two crystallographically independent sets of Cu(II) ions and three types of azido ligands in the different coordination modes ( $\mu$ -1,  $\mu$ -1,1 and  $\mu$ -1,1,3).

The Cu1 cations are coordinated by three azido groups acting as  $\mu$ -1,1 bridging ligands (N3–N4–N5, N3A–N4A–N5A and N6–N7–N8) and one azido group acting as  $\mu$ -1,1,3 bridging ligand (N14–N15–N16). The axial Cu1–N14 bonds [2.847(2) Å] are about 0.8 Å longer than the other five basically equivalent equatorial Cu1–N bonds ( $\approx$  2.0 Å). Two contra-position nitrogen atoms and bond angles of the Cu1 cation are 173.01(8)° and 164.90(8)° respectively [ $\angle$  N3–Cu1–N2 = 173.01(8)°,  $\angle$  N6–Cu1–N1 = 164.90(8)°]. Two border upon nitrogen atoms and the bond angles of the Cu1 cation deviate from 90° [ $\angle$  N3–Cu1–N6 = 95.51(9)°,  $\angle$  N6–Cu1–N2 = 88.93(8)°,  $\angle$  N3–Cu1–N1 = 92.27(8)°,  $\angle$  N2–Cu1–N1 = 84.65(8)°,  $\angle$  N3–Cu1–N14 = 101.55(8)° and  $\angle$  N6–Cu1–N14 = 81.54(7)°]. So the Cu1 cations exhibit slightly distorted-octahedral configurations.

The Cu2 atoms are coordinated in a distorted octahedral environment by one  $\mu$ -1 bridging ligand (N11–N12–N13), one  $\mu$ -1,1 bridging ligand (N6–N7–N8) and two azido groups acting as  $\mu$ -1,1,3 bridging ligands (N14–N15–N16 and N14B–N15B–N16B). The Cu2–N bonds are about 1.995(2)–2.617(2) Å and two contra-position nitrogen atoms and bond angles of the Cu2 cation are about 170–176°. In addition, two border upon nitrogen atoms and the bond angles of the Cu2 cation deviate from 90°. So the Cu2 cations also exhibit the slightly distorted-octahedral configurations.

There are four planes formed by the nitrogen atoms and the Cu(II) cation, and the plane equations are as follows:

Cu1–N1–N2–N3–N6 (plane A):  $1.940x - 0.585y + 24.810z = 1.7206$  ( $R = 0.1438$ );

Cu1A–N1A–N2A–N3A–N6A (plane B):  $1.940x - 0.585y + 24.810z = -1.0428$  ( $R = 0.1438$ );

Cu2–N9–N10–N11–N14 (plane C):  $-2.318x + 0.507y + 25.940z = 4.0481$  ( $R = 0.0550$ );

Cu2A–N9A–N10A–N11A–N14A (plane D):  $-2.318x + 0.507y + 25.940z = -4.9537$  ( $R = 0.0550$ ).

The planes A and B as well as planes C and D are approximately parallel, respectively. The angles between planes A(B) and C(D) are 17.0°, respectively.

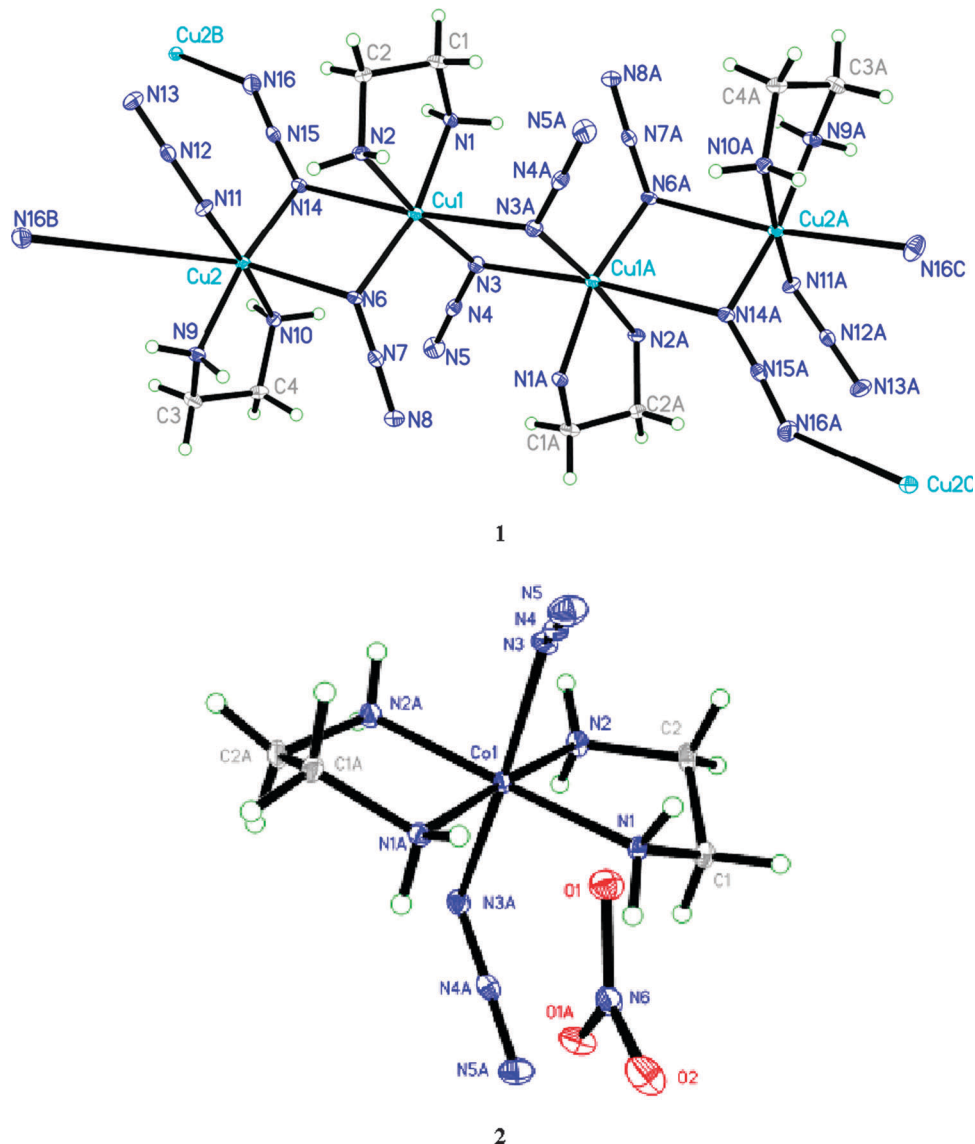


Fig. 2 The molecular structures of **1** and **2**, thermal ellipsoids drawn at the 30% probability level.

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

Bond	Dist.	Bond	Dist.	Bond	Dist.
Cu1–N3	1.990(2)	Cu2–N10	2.0271(19)	N12–N13	1.148(3)
Cu1–N6	1.9954(19)	Cu2–N6	2.617(2)	N14–N15	1.196(3)
Cu1–N2	1.9973(19)	Cu2–N16	2.558(2)	N15–N16	1.154(3)
Cu1–N1	2.0122(19)	N3–N4	1.200(3)	N1–C1	1.482(3)
Cu1–N14	2.847(2)	N4–N5	1.163(3)	N2–C2	1.486(3)
Cu2–N11	1.995(2)	N6–N7	1.194(3)	N9–C3	1.484(3)
Cu2–N14	1.998(2)	N7–N8	1.159(3)	N10–C4	1.480(3)
Cu2–N9	2.027(2)	N11–N12	1.210(3)	C1–C2	1.502(4)
Bond	Angle	Bond	Angle	Bond	Angle
N3–Cu1–N6	95.51(9)	N14–Cu2–N9	170.83(8)	N14A–Cu2A–N9A	98.63(8)
N3–Cu1–N2	173.01(8)	N11–Cu2–N10	176.03(8)	N11A–Cu2A–N10A	178.2(2)
N6–Cu1–N2	88.93(8)	N14–Cu2–N10	88.98(8)	N14A–Cu2A–N10A	108.55(14)
N3–Cu1–N1	92.27(8)	N9–Cu2–N10	83.92(8)	N9A–Cu2A–N10A	110.04(14)
N6–Cu1–N1	164.90(8)	N11–Cu2–N6	87.66(7)	N11A–Cu2A–N6A	123.00(16)
N2–Cu1–N1	84.65(8)	N14–Cu2–N6	87.65(7)	N14A–Cu2A–N6A	177.1(3)
N3–Cu1–N14	101.55(8)	N9–Cu2–N6	87.00(7)	N9A–Cu2A–N6A	122.01(16)
N6–Cu1–N14	81.54(7)	N10–Cu2–N6	93.54(7)	N10A–Cu2A–N6A	133.82(16)

**Table 3** Selected bond lengths (Å) and bond angles (°) for **2**<sup>a</sup>

Bond	Dist.	Bond	Dist.	Bond	Dist.
Co1–N1	1.9521(11)	Co1–N2	1.9688(12)	N6–O2	1.241(2)
Co1–N1#1	1.9521(11)	N1–C1	1.4810(18)	N6–O1#1	1.2590(13)
Co1–N3#1	1.9564(13)	N2–C2	1.4834(17)	N6–O1	1.2590(13)
Co1–N3	1.9564(13)	N3–N4	1.2065(17)	C1–C2	1.513(2)
Co1–N2#1	1.9688(12)	N4–N5	1.1559(18)		
Bond	Angle	Bond	Angle	Bond	Angle
N1–Co1–N1#1	92.61(7)	N3–Co1–N2#1	87.24(5)	N4–N3–Co1	119.12(9)
N1–Co1–N3#1	94.02(5)	N1–Co1–N2	85.58(5)	N5–N4–N3	177.28(15)
N1–Co1–N3	90.45(5)	N3–Co1–N2	88.44(5)	O2–N6–O1#1	120.33(8)
N3A–Co1–N3	173.52(7)	C1–N1–Co1	109.75(8)	N1–C1–C2	106.42(11)
N1–Co1–N2#1	176.96(5)	C2–N2–Co1	109.20(8)	N2–C2–C1	107.28(11)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: #1  $-x + 1, y, -z + 3/2$ .

In **2**, the central cobalt(III) cations are coordinated by two azido groups acting as  $\mu$ -1 bridging ligands (Co1–N3 and Co–N3A) and four N atoms of the bidentate ethylenediamine ligands. The N atoms from two contraposition ethylenediamine ligands (or azido groups) and the central cobalt(III) cation bond angles are  $173$ – $177^\circ$  [ $\angle$ N1–Co1–N2A =  $176.96(5)^\circ$ ,  $\angle$ N3A–Co1–N3 =  $173.52(7)^\circ$ ]. Nitrogen atoms from two border upon ethylenediamine ligands (or azido groups) and the cobalt(III) cation bond angles all deviate from  $90^\circ$ , and they are  $92.61(7)^\circ$  ( $\angle$ N1–Co1–N1A),  $94.02(5)^\circ$  (N1–Co1–N3A) and  $90.45(5)^\circ$  ( $\angle$ N1–Co1–N3), respectively. The distances of Co(III)–N are  $1.9521(11)$ – $1.9688(12)$  Å, and which are all about equal. Consequently the above data demonstrates that the Co(III) cations exhibit slightly distorted-quadrilateral configurations.

The six coordination-atoms and the central cobalt(III) cation can form a plane and the plane equation is as follows:

Co1–N1–N2–N1A–N2A–N6 (plane E):  $5.323x + 0.000y + 7.812z = 8.5205$  ( $R = 0.0274$ ).

Weak N–H...N hydrogen bonds between the azido groups and en ligands occurred in **1**. While in **2**, the azido-groups, en ligands and nitrate ions can form weak N–H...N, N–H...O and C–H...N hydrogen bonds (see the ESI<sup>†</sup>). It can be seen from the packing diagram that all of these intermolecule hydrogen bonds are to extend the structure into a 3D supermolecular structure, and to make an important contribution to enhance the thermal stability of the compounds.

### Thermal decomposition

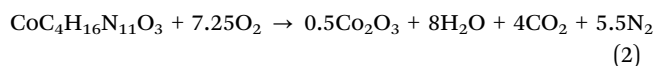
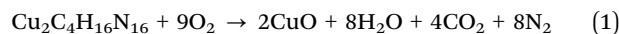
In order to investigate the thermal behaviors of the title compounds, the DSC and TG-DTG curves (with a linear heating rate of  $5 \text{ K min}^{-1}$  in  $\text{N}_2$  gas flowing at a rate of  $20 \text{ ml min}^{-1}$ ) are shown in Fig. 3. In **1** and **2**, the melting point was not observed in the DSC curves. In **1**, the exothermic stages were two main decomposition stages, and the peak temperatures were at  $474.95 \text{ K}$  and  $598.25 \text{ K}$ , respectively. The TG-DTG curves showed that there was a mass loss of  $49.1\%$  in the first stage, where the largest rate was reached at  $462 \text{ K}$ , with a mass loss percentage of  $12.2\% \text{ min}^{-1}$ . The second mass loss stage was a very slow stage and the mass loss was  $13.2\%$ . In **2**, two main successive exothermic processes appeared in the range from  $450 \text{ K}$  to

$650 \text{ K}$ , with peak temperatures of  $491.25 \text{ K}$  and  $609.35 \text{ K}$ , respectively. The TG-DTG curves show that there were two mass losses of  $44.2\%$  and  $12.2\%$ , and the largest rate was reached at  $492 \text{ K}$ , with a mass loss percentage of  $49.7\% \text{ min}^{-1}$ .

### Energies of combustion and enthalpies of formation

In order to study the energies of combustion ( $\Delta H = Q_p$ ) and the enthalpies of formation ( $\Delta_f H^\circ_{298}$ ) of the title compounds, constant-volume energies of combustion ( $Q_v$ ) of **1** and **2** were measured by oxygen bomb calorimetry and were  $-6.82 \text{ MJ kg}^{-1}$  and  $-3.25 \text{ MJ kg}^{-1}$ , respectively.

The bomb combustion reaction equations might be as follows:



And the energies of combustion are as follows:

$$\Delta H(\mathbf{1}) = Q_p = Q_v + \Delta nRT = -2840.46 \text{ kJ mol}^{-1} = -6.84 \text{ MJ kg}^{-1} \quad (3)$$

$$\Delta H(\mathbf{2}) = Q_p = Q_v + \Delta nRT = -1063.13 \text{ kJ mol}^{-1} = -3.26 \text{ MJ kg}^{-1} \quad (4)$$

So the energies of combustion for **1** and **2** were  $-6.84 \text{ MJ kg}^{-1}$  and  $-3.26 \text{ MJ kg}^{-1}$ , respectively. The literature<sup>45</sup> reported energies of combustion for RDX, HMX and TNT were  $-9.60 \text{ MJ kg}^{-1}$ ,  $-9.44$  to  $-9.88 \text{ MJ kg}^{-1}$  and  $-15.22 \text{ MJ kg}^{-1}$ , respectively. Consequently, the energies of combustion of **1** and **2** were lower than that of RDX, HMX and TNT.

These two metal coordination complexes should have relatively thermodynamically stable structures. The standard enthalpies of formation of **1** and **2** were back calculated from the energies of combustion on the basis of eqn (1) and (2), and Hess' Law as applied in thermochemical eqn (5) and (6). With the known enthalpies of formation of copper oxide ( $\Delta_f H^\circ_{298} [\text{CuO}(s)] = -155.2 \text{ kJ mol}^{-1}$ ), cobalt(III) oxide ( $\Delta_f H^\circ_{298} [\text{Co}_2\text{O}_3(s)] = -653.1 \text{ kJ mol}^{-1}$ ), carbon dioxide ( $\Delta_f H^\circ_{298} [\text{CO}_2(g)] = -393.5 \text{ kJ mol}^{-1}$ ) and water

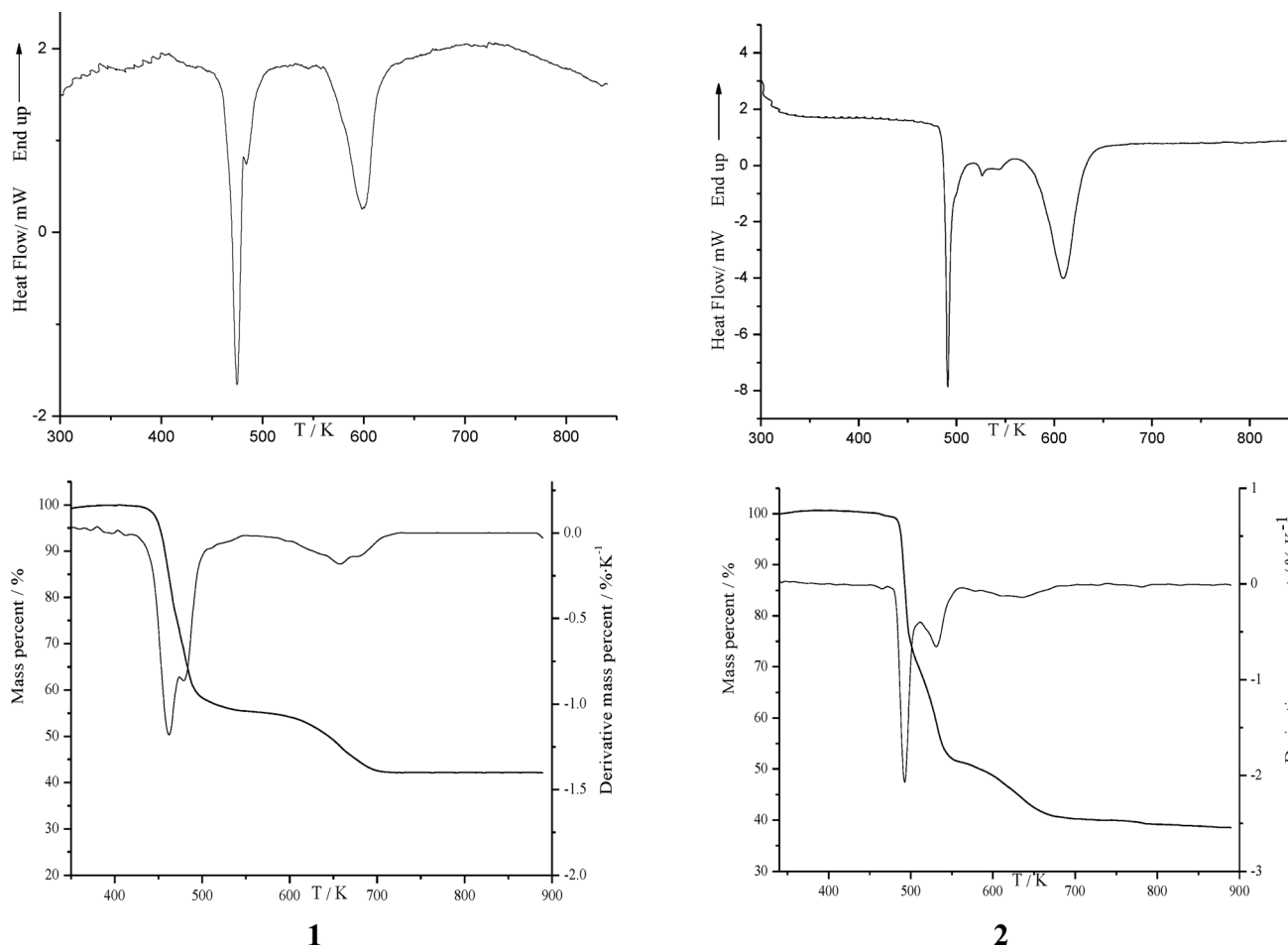


Fig. 3 The DSC curves (top) and TG-DTG curves (bottom) under a N<sub>2</sub> atmosphere with a heating rate of 5 K min<sup>-1</sup>.

( $\Delta_f H^\circ_{298} [\text{H}_2\text{O}(l)] = -285.8 \text{ kJ mol}^{-1}$ ), the enthalpies of formation of **1** and **2** can now be calculated as:

$$\Delta_f H^\circ_{298}(\mathbf{1}) = 2\Delta_f H^\circ(\text{CuO}, s) + 8\Delta_f H^\circ(\text{H}_2\text{O}, l) + 4\Delta_f H^\circ(\text{CO}_2, g) - \Delta_c H^\circ(\mathbf{1}, s) = -1330.34 \text{ kJ mol}^{-1} \quad (5)$$

$$\Delta_f H^\circ_{298}(\mathbf{2}) = 0.5\Delta_f H^\circ(\text{Co}_2\text{O}_3, s) + 8\Delta_f H^\circ(\text{H}_2\text{O}, l) + 4\Delta_f H^\circ(\text{CO}_2, g) - \Delta_c H^\circ(\mathbf{2}, s) = -3123.82 \text{ kJ mol}^{-1} \quad (6)$$

### Non-isothermal kinetics analysis

The Kissinger method<sup>46</sup> and Ozawa method<sup>47</sup> are widely used to determine the Arrhenius Equation. The Kissinger eqn (7) and Ozawa eqn (8) are as follows, respectively:

$$\ln \beta/T_p^2 = \ln [RA/E_a] - E_a/(RT_p) \quad (7)$$

$$\log \beta = \log [AE_a/RG(x)] - 2.315 - 0.4567 E_a/RT_p \quad (8)$$

$T_p$  is the peak temperature in K.  $A$  is the pre-exponential factor in s<sup>-1</sup>.  $E$  is the apparent activation energy in kJ mol<sup>-1</sup>.  $R$  is the gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>).  $\beta$  is the linear heating rate in K min<sup>-1</sup> and  $G(x)$  is reaction mechanism function.

Based on the first exothermic peak temperatures measured with four different heating rates of 5, 10, 15 and 20 K min<sup>-1</sup>, the

Kissinger method and Ozawa method were applied to study the kinetics parameters of the title compounds. From the original data, the apparent activation energy  $E_k$  ( $E_o$ ), pre-exponential factor  $A_k$ , linear correlation coefficient  $R_k$  ( $R_o$ ) were determined and are shown in Table 4.

Accordingly, the Arrhenius Equations of the title compounds can be expressed as follows: ( $E$  is the average of  $E_k$  and  $E_o$ )  $\ln k = 6.147 - 80.28 \times 10^3/RT$  for **1** and  $\ln k = 3.152 - 57.25 \times 10^3/RT$  for **2**.

### Calculation of critical temperature of thermal explosion, $\Delta S^\ddagger$ , $\Delta H^\ddagger$ and $\Delta G^\ddagger$

The values of the peak temperatures [corresponding to  $\beta \rightarrow 0$  ( $T_{p0}$ )], obtained according to eqn (9),<sup>48</sup> were 406.55 K for **1** and 409.35 K for **2**, where  $a$ ,  $b$  and  $c$  are coefficients.

$$T_{pi} = T_{p0} + a\beta + b\beta^2 + c\beta^3 \quad (9)$$

The corresponding critical temperatures of thermal explosion ( $T_b$ ) were 425.28 K for **1** and 437.1 K for **2**, obtained using eqn (10).<sup>48</sup>

$$T_b = \frac{E - \sqrt{E^2 - 4ERT_{p0}}}{2R} \quad (10)$$



**Table 4** The peak temperatures of the first main exotherms at different heating rates and the chemical kinetics parameters

Compounds	1	2
Heating rates $\beta$ (K min <sup>-1</sup> ) 5, 10, 15, 20	Peak temperatures $T_p$ (K) 474.95, 498.75, 500.05, 500.95	491.25, 517.85, 523.15, 541.15
<b>Kissinger method</b> $E_k$ (kJ mol <sup>-1</sup> ), $\ln A_k$ , $R_k$	78.35, 6.147, -0.8952	54.50, 3.152, -0.9777
<b>Ozawa method</b> $E_o$ (kJ mol <sup>-1</sup> ), $R_o$	82.21, -0.9114	59.95, -0.9833

The entropies of activation ( $\Delta S^\ddagger$ ), enthalpies of activation ( $\Delta H^\ddagger$ ), and free energies of activation ( $\Delta G^\ddagger$ ) of the decomposition reaction of **1** and **2** (corresponding to  $T = T_{p0}$  and  $A = A_k$ ), obtained using eqn (11)–(13),<sup>48</sup> were -204.70 kJ mol<sup>-1</sup>, 76.90 J (K mol)<sup>-1</sup>, and 160.12 kJ mol<sup>-1</sup> for **1**, and -229.65 kJ mol<sup>-1</sup>, 53.85 J (K mol)<sup>-1</sup>, and 147.86 kJ mol<sup>-1</sup> for **2**, respectively.

$$A = \frac{k_B T}{h} e^{\Delta S^\ddagger / R} \quad (11)$$

$$\Delta H^\ddagger = E - RT \quad (12)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (13)$$

Where  $k_B$  is the Boltzmann constant ( $1.381 \times 10^{-23}$  J/K) and  $h$  is the Planck constant ( $6.626 \times 10^{-34}$  J s).

### Sensitivity tests

On the basis of the China National Military Standard, the impact and flame sensitivity were determined.<sup>49</sup>

The impact sensitivity was determined using Fall Hammer Apparatus. The compound (30 mg) was placed between two steel poles and was hit by a 10.0 kg drop hammer. The test results showed that the 50% firing heights ( $h_{50}$ ) were 8.0 cm (7.84 J) for **1** and 15.5 cm (15.19 J) for **2**.

The friction sensitivity was determined on a MGY-1 pendular friction sensitivity apparatus by a standard procedure using 20 mg of the sample. The compound was compressed between two steel poles with mirror surfaces at a pressure of 1.96 MPa, it was then hit horizontally with a 1.5 kg hammer from a 90° angle – the firing rates were 76% for **1** and 36% for **2**.

The flame sensitivity was determined by following a standard method, in which the sample was ignited by a standard black powder pellet. The compound (20 mg) was compacted into a copper cap under the press of 58.8 MPa and was ignited by a standard black powder pellet. The test results showed that the 50% firing height ( $h_{50}$ ) of **1** was 15.0 cm, and there was no fire at the 6 cm minimum height of **2**.

Therefore, compared to cadmium(II) ethylenediamine azide ([Cd(en)(N<sub>3</sub>)<sub>2</sub>]<sub>*n*</sub>),<sup>19</sup> **1** had much higher flame and friction sensitivities, however, it had a lower impact sensitivity. However, compared to nickel(II) hydrazine azide,<sup>22</sup> **1** had higher impact and friction sensitivities, and a lower flame sensitivity.

### Physicochemical properties

The physicochemical properties of **1** and **2** are tabulated in Table 5. These compounds are nitrogen-rich materials with

**Table 5** Physicochemical properties of **1** and **2**

Compounds	1	2
$T_d$ (K) <sup>a</sup>	474.95, 598.25	491.25, 609.35
N (%) <sup>b</sup>	53.95	47.38
$\Omega$ (%) <sup>c</sup>	-69.33	-68.88
$E$ (kJ mol <sup>-1</sup> ) <sup>d</sup>	80.28	57.25
$\Delta H^\circ$ (kJ mol <sup>-1</sup> ) <sup>e</sup>	-2840.46	-1063.13
$\Delta_f H^\circ_{298}$ (kJ mol <sup>-1</sup> ) <sup>f</sup>	-1330.34	-3123.82
$T_{p0}$ (K)	406.55	409.35
$T_b$ (K)	433.89	437.1
$\Delta S^\ddagger$ (kJ mol <sup>-1</sup> )	-204.70	-229.65
$\Delta H^\ddagger$ (J (K mol) <sup>-1</sup> )	76.90	53.85
$\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )	160.12	147.86
Impact sensitivity (J)	7.84	15.19

<sup>a</sup> Thermal degradation/DSC main exothermic peak. <sup>b</sup> Nitrogen content. <sup>c</sup> Oxygen balance. <sup>d</sup> Activation energy. <sup>e</sup> Experimental energy of combustion. <sup>f</sup> Molar enthalpy of formation.

their nitrogen content reaching more than 47%. They have a better oxygen balance than TNT ( $\Omega = -74.0\%$ ).

## Conclusions

Two new high-nitrogen and environmentally-friendly energetic compounds of copper(II) ethylenediamine (en) azide and cobalt(III) ethylenediamine azide, [Cu<sub>2</sub>(en)<sub>2</sub>(N<sub>3</sub>)<sub>4</sub>]<sub>*n*</sub> (**1**) and Co(en)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>(NO<sub>3</sub>) (**2**), were synthesized and characterized. The crystal structures show that the Cu(II) ion and Co(III) ion are six-coordinated in a distorted octahedral geometry. In addition, the azido-groups display different coordination modes. The experiment found that the energies of combustion and enthalpies of formation of **1** and **2** were -6.82 MJ kg<sup>-1</sup>, -3.25 MJ kg<sup>-1</sup> and -1330.34 kJ mol<sup>-1</sup>, -3123.82 kJ mol<sup>-1</sup>, respectively. The non-isothermal kinetics analysis results indicated that the Arrhenius equation can be expressed as follows:  $\ln k = 6.147 - 80.28 \times 10^3/RT$  for **1** and  $\ln k = 3.152 - 57.25 \times 10^3/RT$  for **2**. The critical temperature of thermal explosion ( $T_b$ ) was 425.28 K for **1** and 437.1 K for **2**. The entropies of activation ( $\Delta S^\ddagger$ ), enthalpies of activation ( $\Delta H^\ddagger$ ), and free energies of activation ( $\Delta G^\ddagger$ ) of the decomposition reaction of **1** and **2** were -204.70 kJ mol<sup>-1</sup>, 76.90 J (K mol)<sup>-1</sup>, and 160.12 kJ mol<sup>-1</sup> for **1**, and -229.65 kJ mol<sup>-1</sup>, 53.85 J (K mol)<sup>-1</sup>, and 147.86 kJ mol<sup>-1</sup> for **2**, respectively. The impact and flame sensitivity results showed that the 50% firing heights were 8.0 cm (7.84 J), 15.0 cm (15.19 J) for **1**, and 15.5 cm, and no fire for **2**, respectively. In conclusion, the results of all these studies have shown that **1** and **2** have a potential application as energetic materials in the near future.

**Table 6** Crystal data and structure refinement for **1** and **2**<sup>a</sup>

Compounds	<b>1</b>	<b>2</b>
CCDC	893075	893076
Empirical formula	Cu <sub>2</sub> C <sub>4</sub> H <sub>16</sub> N <sub>16</sub>	CoC <sub>4</sub> H <sub>16</sub> N <sub>11</sub> O <sub>3</sub>
Formula mass	415.40	325.21
Crystal dimensions (mm)	0.54 × 0.39 × 0.22	0.39 × 0.33 × 0.29
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c
Z	16	4
a, b, c (Å)	17.665(4), 6.3279(14), 26.063(6)	13.671(4), 9.447(2), 9.343(3)
β (°)	100.725(3)	100.349(3)
h, k, l	−24−21, −8−8, −35−35	−19−19, −12−13, −13−13
Temperature (K)	293(2)	153(2)
Unit cell dimensions V(Å <sup>3</sup> )	2862.4(11)	1187.0(5)
D <sub>c</sub> (g cm <sup>−3</sup> )	1.928	1.820
μ (Mo K <sub>α</sub> ) (mm <sup>−1</sup> )	2.999	1.476
F(0 0 0)	1680	672
θ Range (°)	3.07–29.12	2.63–31.00
Max. and min. transmission	0.5557, 0.2943	0.6734, 0.6004
Measured reflections	11765	5540
Unique data	3768 (R <sub>int</sub> = 0.0325)	1868 (R <sub>int</sub> = 0.0295)
R <sub>1</sub> , wR <sub>2</sub> [I > 2σ(I)]	R <sub>1</sub> = 0.0326, wR <sub>2</sub> <sup>b</sup> = 0.0800	R <sub>1</sub> = 0.0281, wR <sub>2</sub> <sup>c</sup> = 0.0748
R <sub>1</sub> , wR <sub>2</sub> (all data)	R <sub>1</sub> = 0.0448, wR <sub>2</sub> <sup>b</sup> = 0.0872	R <sub>1</sub> = 0.0325, wR <sub>2</sub> <sup>c</sup> = 0.0778
Goodness of fit	0.998	1.001
δρ <sub>max</sub> , δρ <sub>min</sub> (e Å <sup>−3</sup> )	1.408, −0.502	0.474, −0.588

$$^a wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}, P = (F_o^2 + 2F_c^2)/3. ^b w = 1/[\sigma^2(F_o^2) + (0.0516 P)^2 + 0.8150 P]. ^c w = 1/[\sigma^2(F_o^2) + (0.0485 P)^2 + 0.1600 P].$$

## Experimental

### Materials and physical techniques

All reagents and solvents were analytically pure commercial products. The starting material, sodium azide, is a commercial product and was refined by recrystallization before use.

Elemental analyses were performed on a Flash EA 1112 full-automatic trace element analyzer. The FT-IR spectra were recorded on a Bruker Equinox 55 infrared spectrometer (KBr pellets) in the range of 4000–400 cm<sup>−1</sup> with a resolution of 4 cm<sup>−1</sup>. DSC and TG-DTG measurements were carried out by using a Pyris-1 differential scanning calorimeter and Pyris-1 thermogravimetric analyzer (Perkin Elmer, USA) under a dry nitrogen atmosphere with a flow rate of 20 ml min<sup>−1</sup>. The conditions for the thermal analyses were as follows: for Pyris-1 DSC and Pyris-1 TGA (USA), the crystal sample was powdered and put into the aluminum pans and open platinum pans, respectively, with a linear heating rate of 10 K min<sup>−1</sup> from 300 K to 850 K. The combustion heats of the title compounds were measured by oxygen bomb calorimetry (Parr 6200, USA).

### Synthesis of **1** and **2**

**1** and **2** were prepared as follows: a solution containing Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (2.42 g, 10 mmol) or Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2.91 g, 10 mmol) in deionized water (30 ml) was charged into a glass reactor with a thermo-water bath. The reaction solution was stirred with a mechanical agitator and heated to 60–70 °C. Ethylenediamine (0.6 g, 10 mmol for **1** and 1.2 g, 20 mmol for **2**) and sodium azide (1.30 g, 20 mmol) dissolved in 20 ml of deionized water were added to the Cu(NO<sub>3</sub>)<sub>2</sub> or Co(NO<sub>3</sub>)<sub>2</sub> aqueous solution over 30 min with continuous stirring, with a temperature maintained at 60–70 °C. Then the solution was cooled naturally to room temperature under stirring.

The precipitate was collected by filtration, washed with ethanol, dried in an explosion-proof water-bath dryer. The yields were 62% for **1** and 45% for **2**.

Surprisingly, the Co(II) is oxidized, forming Co(III) with the en group of **2**.

Elemental analysis: **1** (%): calculated: C 11.57; H 3.88; N 53.95; found: C 11.64; H 3.86; N 53.98; **2** (%): calculated: C 14.77; H 4.96; N 47.38; found: C 14.81; H 4.86; N 47.32.

IR (cm<sup>−1</sup>, KBr pellets): **1**: 3566, 3311, 3133, 2084, 1584, 1289, 1036, 696, 535; **2**: 3555, 3271, 3126, 2086, 2021, 1571, 1456, 1315, 1052, 771, 671, 624.

### X-ray data collection and structure refinement

Single crystals suitable for X-ray measurement were obtained by a hydrothermal method. The products were then recrystallized with deionized water at room temperature for two weeks. The X-ray diffraction data collection was performed on a Rigaku AFC-10/Saturn 724<sup>+</sup> CCD detector diffractometer with graphite monochromated Mo K<sub>α</sub> radiation (λ = 0.071073 nm) with multi-scan modes. The structures were solved by direct methods using SHELXS-97 (Sheldrick, 1990)<sup>50</sup> and refined by the full-matrix least-squares method on F<sup>2</sup> with SHELXL-97 (Sheldrick, 1997).<sup>51</sup> And all non-hydrogen atoms were obtained from the difference Fourier map and subjected to anisotropic refinement by full-matrix least squares on F<sup>2</sup>. Detailed information concerning the crystallographic data collection and structure refinements are summarized in Table 6.

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## References

- 1 T. M. Klapötke and G. Holl, *Green Chem.*, 2001, **3**, G75.
- 2 T. M. Klapoetke, F. A. Martin and J. Stierstorfer, *Chem.–Eur. J.*, 2012, **18**, 1487.
- 3 T. M. Klapoetke, D. G. Piercey and J. Stierstorfer, *Chem.–Eur. J.*, 2011, **17**, 13068.
- 4 T. M. Klapötke, F. A. Martin and J. Stierstorfer, *Angew. Chem., Int. Ed.*, 2011, **50**, 4227.
- 5 T. M. Klapötke and D. G. Piercey, *Inorg. Chem.*, 2011, **50**, 2732.
- 6 T. M. Klapötke and C. Miró Sabaté, *Z. Anorg. Allg. Chem.*, 2009, **635**, 1812.
- 7 T. M. Klapötke, C. M. Sabaté and J. M. Welch, *Heteroat. Chem.*, 2009, **20**, 35.
- 8 T. M. Klapötke, J. Stierstorfer and B. Weber, *Inorg. Chim. Acta*, 2009, **362**, 2311.
- 9 H. Gao and J. M. Shreeve, *Chem. Rev.*, 2011, **111**, 7377.
- 10 R. Wang, Y. Guo, R. Sa and J. M. Shreeve, *Chem.–Eur. J.*, 2010, **16**, 8522.
- 11 Y. H. Joo and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2010, **49**, 7320.
- 12 Y. H. Joo, H. Gao, Y. Zhang and J. M. Shreeve, *Inorg. Chem.*, 2010, **49**, 3282.
- 13 Y. Guo, G. H. Tao, Z. Zeng, H. Gao, D. A. Parrish and J. M. Shreeve, *Chem.–Eur. J.*, 2010, **16**, 3753.
- 14 Y. C. Li, C. Qi, S. H. Li, H. J. Zhang, C. H. Sun, Y. Z. Yu and S. P. Pang, *J. Am. Chem. Soc.*, 2010, **132**, 12172.
- 15 C. Qi, S. H. Li, Y. C. Li, Y. Wang, X. K. Chen and S. P. Pang, *J. Mater. Chem.*, 2011, **21**, 3221.
- 16 J. Giles, *Nature*, 2004, **427**, 580.
- 17 B. D. Wu, L. Yang, S. W. Wang, T. L. Zhang, J. G. Zhang, Z. N. Zhou and K. B. Yu, *Z. Anorg. Allg. Chem.*, 2011, **637**, 450.
- 18 B. D. Wu, S. W. Wang, L. Yang, T. L. Zhang, J. G. Zhang, Z. N. Zhou and K. B. Yu, *Eur. J. Inorg. Chem.*, 2011, 2616.
- 19 L. Yang, B. D. Wu, T. L. Zhang, Z. H. Liu and J. G. Zhang, *Propellants, Explos., Pyrotech.*, 2010, **35**, 521.
- 20 Q. Ma, M. Zhu, L. Lu, S. Feng and J. Yan, *Inorg. Chim. Acta*, 2011, **370**, 102.
- 21 D. Bose, S. H. Rahaman, G. Mostafa, R. D. B. Walsh, M. J. Zaworotko and B. K. Ghosh, *Polyhedron*, 2004, **23**, 545.
- 22 S. G. Zhu, D. W. Xu, S. J. Cao, J. Y. Mu and L. G. Chen, *Chem. Res. Chin. Univ.*, 2005, 18.
- 23 D. L. Sheng, F. E. Ma, Y. F. Zhang, Y. H. Zhu, L. K. Chen and B. Yang, *Chin. J. Energ. Mater.*, 2009, 694.
- 24 E. A. Bykova, S. P. Khramenko and S. A. Gromilov, *J. Struct. Chem.*, 2012, **53**, 184.
- 25 J. Chun, Y. Lee, S. Pyo, C. Im, S. J. Kim, H. Yun and J. Do, *Bull. Korean Chem. Soc.*, 2009, **30**, 1603.
- 26 S. Farhadi and Z. Roostaeei-Zaniyani, *Polyhedron*, 2011, **30**, 971.
- 27 M. L. Feng, P. X. Li, K. Z. Du and X. Y. Huang, *Eur. J. Inorg. Chem.*, 2011, 3881.
- 28 X. Liu, X. H. Yin and F. Zhang, *Z. Naturforsch., B: Chem. Sci.*, 2010, **65**, 1451.
- 29 H. Luehmann, C. Naether and W. Bensch, *Z. Anorg. Allg. Chem.*, 2011, **637**, 1007.
- 30 K. R. Ma, J. Shi, D. J. Zhang and J. N. Xu, *J. Mol. Struct.*, 2012, **1013**, 138.
- 31 W. Niu, D. Shi, J. Zhao, X. Cai and L. Chen, *Inorg. Chem. Commun.*, 2012, **17**, 79.
- 32 O. O. E. Onawumi, O. O. P. Faboya, O. A. Odunola, T. K. Prasad and M. V. Rajasekharan, *Polyhedron*, 2011, **30**, 725.
- 33 C. Y. Pan, S. Hu, D. G. Li, O. Y. Ping, F. H. Zhao and Y. Y. Zheng, *Dalton Trans.*, 2010, **39**, 5772.
- 34 K. S. Rejitha, T. Ichikawa and S. Mathew, *J. Therm. Anal. Calorim.*, 2012, **107**, 887.
- 35 M. Singh, A. K. Pandey, R. J. Butcher and N. K. Singh, *Polyhedron*, 2009, **28**, 461.
- 36 A. I. Smolentsev, A. V. Ermolaev and Y. V. Mironov, *J. Mol. Struct.*, 2012, **1014**, 57.
- 37 D. Venegas-Yazigi, K. A. Brown, A. Vega, R. Calvo, C. Aliaga, R. C. Santana, R. Cardoso-Gil, R. Kniep, W. Schnelle and E. Spodine, *Inorg. Chem.*, 2011, **50**, 11461.
- 38 X. Wang, F. Luo and W. T. Gao, *Chin. J. Inorg. Chem.*, 2009, **25**, 154.
- 39 Q. Wu, J. He, Q. X. Han, W. H. Yang and J. P. Wang, *Chin. J. Struct. Chem.*, 2010, **29**, 1219.
- 40 L. Yu, J. P. Liu, J. P. Wang and J. Y. Niu, *Chem. Res. Chin. Univ.*, 2009, **25**, 426.
- 41 J. Zhou, Y. Zhang, M. H. Zhang, Z. X. Lei and J. Dai, *Z. Naturforsch., B: Chem. Sci.*, 2009, **64**, 504.
- 42 L. Yang, J. Zhang, T. L. Zhang, J. G. Zhang and Y. Cui, *J. Hazard. Mater.*, 2009, **164**, 962.
- 43 Z. H. Liu, T. L. Zhang, J. G. Zhang and S. Z. Wang, *J. Hazard. Mater.*, 2008, **154**, 832.
- 44 Z. H. Liu, T. L. Zhang, J. G. Zhang, L. Yang, J. Zhang and Y. Zang, *Chin. J. Energ. Mater.*, 2008, 663.
- 45 Y. X. Ou, *Beijing Institute of Technology*, Explosives, China, 2006.
- 46 H. E. Kissinger, *Anal. Chem.*, 1957, **29**, 1702.
- 47 T. Ozawa, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 1881.
- 48 J. H. Yi, F. Q. Zhao, B. Z. Wang, Q. Liu, C. Zhou, R. Z. Hu, Y. H. Ren, S. Y. Xu, K. Z. Xu and X. N. Ren, *J. Hazard. Mater.*, 2010, **181**, 432.
- 49 Z. T. Liu and Y. L. Lao, *Beijing Institute of Technology*, China, 1995.
- 50 G. M. Sheldrick, *SHELXS 97, Program for the Solution of Crystal Structures*, University of Gottingen, Germany, 1990.
- 51 G. M. Sheldrick, *SHELXL 97, Program for Crystal Structure Refinement from Diffraction Data*, University of Gottingen, Germany, 1997.