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The search for new powerful energetic transition metal complexes based on 3,3′-dinitro-5,5′-bis-1,2,4-triazole-1,1′-diolate anion: a DFT study

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Abstract In this study, employing a new high oxygen balance energetic 3,3′-dinitro-5,5′-bis-1,2,4-triazole-1,1′-diolate anion (DNBTDO) as the bidentate ligand, NH_3 and NH_2NO_2 as short energetic ligands, and Cu/Ni as the metal atoms, two series of novel energetic metal complexes were computationally designed. Their structures and properties were studied by density functional theory, electrostatic potential data, and molecular mechanics methods. The results showed that the designed metal complexes have high detonation performance and acceptable sensitivity: $Cu/Ni(DNBTDO)(NH_2NO_2)_2$ (A3/B3) have better detonation properties and lower sensitivity than the most powerful CHNO explosive hexanitrohexaazaisowurtzitane, $Cu/Ni(DNBTDO)(NH_3)(NH_2NO_2)$ (A2/B2) have comparable energetic performance and sensitivity with 1,3,5,7-tetranitro-1,3,5,7-tetrazocane, $Ni(DNBTDO)(NH_3)_2$ (B1) has comparative energy level and sensitivity with 1,3,5-trinitro-1,3,5-triazinane. These five energetic metal complexes may be attractive to energetic materials researchers. Besides, both the energetic ligands and metal atoms could have a great influence on the structures, heats of formation, detonation properties, and stability of energetic metal complexes, and the effects are coupled with each other. This study may be helpful in the search for and development of new improved energetic materials.

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Introduction

To meet the on-going and increased need for advanced high energy materials in national defense, military, and civil applications, more and more theoretical and experimental investigations have been done to design, synthesize, and develop new energetic materials with novel structures or better overall performance in the 21st century. Lately, due to the obviously different structures to traditional CHNO energetic compounds, high-energy metal-organic frameworks (HE-MOFs) are found to have high density and hardness, good thermal stability, and mechanical strength, as well as other advantages [1–10]. These make HE-MOFs attracted considerable attention of energetic materials scientists. Thus, HE-MOFs have experienced and obtained quick development in the past several years, since two energetic hydrazine-perchlorate 1D MOFs $[(Ni(NH_2NH_2)_5(ClO_4)_2)n$ (NHP), and $(Co(NH_2NH_2)_5(ClO_4)_2)n$ (CHP)] were synthesized and reported [1].

Many studies were done to develop new 1D, 2D, and 3D energetic MOFs by using different energetic ligands and metal atoms. For example, first of all, using nitrogen-rich energetic compounds like 4-amino-1,2,4-triazole [ATZ, nitrogen content (N%) = 66.6%] [2], 3-hydrazino-4-amino-1,2,4-triazole(HATr, N% = 73.6%) [3, 4] as ligands, some 1D energetic complexes like $\{Zn(ATZ)_3\}(PA)_2 \cdot 2.5H_2O\}_n$, $[Cd(HATr)_2(ClO_4)_2]_n$ and $[Cd_2(HATr)_4(N_3)_4 \cdot H_2O]_n$ were synthesized successfully. It is found that several of them have high density and heat of detonation (ΔH_{det}) but they are very sensitive, while the rest possess mediocre energetic performance. Then, to decrease the sensitivity of 1D MOFs, some 2D energetic MOFs such as

[Cu(pn)(N$_3$)$_2$]$_n$ and [Cd(DAT)(N$_3$)$_2$]$_n$ were prepared based on ligands like 1,2-diaminopropane (pn) [5] and 1,5-diaminotetrazole (DAT) [6], respectively. Compared to the previous 1D complexes, these 2D MOFs do have lower sensitivities toward physical stimuli, and higher thermal stability. However, their ΔH_{det} are also decreased obviously. Lately, some 3D energetic MOFs have been developed, such as the [Cu(atzr)$_3$(NO$_3$)$_2$]$_n$ (atzr = 4,4′-azo-1,2,4-triazole) [7], [Co$_9$(bta)$_{10}$(H$_2$bta)$_2$(H$_2$O)$_{10}$]$_n$·[22H$_2$O]n [H$_2$bta = N,N-bis(1H-tetrazole-50yl)-amine] [8] and [Cu$_4$Na(Mtta)$_5$(CH$_3$CN)]$_n$ (Mtta = 5-methyltetrazole) [9]. Generally, these 3D MOFs have higher density and ΔH_{det} but lower sensitivity than 2D complexes. However, compared to the famous traditional organic high-energy compounds like HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane) or RDX (1,3,5-trinitro-1,3,5-triazinane), most of these 1D, 2D, and 3D energetic MOFs possess relatively low detonation properties [such as the detonation pressure (the pressure on the shock wave Chapman–Jouguet surface when an explosive detonating, P) and detonation velocity (the velocity at which the shock wave front travels through a detonated explosive, D)], only a few energetic MOFs have P more than 40 GPa and D more than 9 km/s. One important reason for this is that the energetic ligands used in them have low energy, and the energy of MOFs are mainly from the ligands. For instance, ATZ, HATr, atzr, H$_2$bta and Mtta all have negatvie oxygen balance (OB) values and low densities, while these two parameters are two key factors that have great effects on the energetic performance of high-energy compounds. In general, the higher the OB (the ideal value is zero) and density are, the better the energetic performance. Thus, to improve the energy level of energetic MOFs, an alternative strategy is to use the appropriate energetic ligand, which has relatively higher OB and density.

Recently, Dippold and Klapötke synthesized a new energetic ionic 3,3′-dinitro-5,5′-bis-1,2,4-triazole-1,1′-diolate anion [DNBTDO, N% = 43.7%, oxygen content (O%) = 37.5%, as shown in Fig. 1] [11], its corresponding molecule is 3,3′-dinitro-5,5′-bis-1,2,4-triazole-1,1′-diol. This compound not only has higher OB (−18.6%), density (1.92 g/cm^3) and detonation properties (D = 8.7 km/s, P = 36.2 GPa) than RDX, but also has lower impact sensitivity (10 J) and friction sensitivity (360 N) than RDX. Furthermore, its organic ionic derivatives (composed of DNBTDO and NH$_4^+$, N$_2$H$_5^+$, NH$_3$OH$^+$, and three other C$_a$H$_b$N$_c^+$) have also comparative detonation properties (D = 8.1–8.9 km/s, P = 26.3–39.0 GPa) to RDX, comparable or better thermal stability (thermal decomposition temperatures = 217–329 °C) than RDX and HMX, and obviously lower sensitivity (impact sensitivity ≥15 J, friction sensitivity ≥324 N) than RDX and HMX. This shows the high value of DNBTDO, and may be a good energetic ligand used for constructing new energetic metal complexes, further used for designing novel high-energy MOFs.

Thus, in the present study, we thought to computationally design novel high-energy metal complexes by employing DNBTDO and Cu/Ni as the energetic chelating ligand and metal atoms, respectively. Furthermore, ammonia (NH$_3$) and nitramide (NH$_2$NO$_2$) were also selected as complexing agents for three reasons: (1) both of them could involve the lone pair electron on combining them to metal atoms, and offer more than six N atoms which could coordinate to the copper/Ni atoms through universal coordinated modes. (2) The NH$_3$ would be helpful in generating hydrogen bonds and thus improving the density and stability. (3) NH$_2$NO$_2$ would be useful for increasing the OB and energy level (containing one nitro group) without increasing the sensitivity obviously (containing one NH$_2$ also). In all, two series of novel energetic metal complexes were computationally designed by the above method, as shown in Fig. 2: [A1: Cu(DNBTDO)(NH$_3$)$_2$, A2: Cu(DNBTDO)(NH$_3$)(NH$_2$NO$_2$), and A3: Cu(DNBTDO)(NH$_2$NO$_2$)$_2$; B1: Ni(DNBTDO)(NH$_3$)$_2$, B2: Ni(DNBTDO)(NH$_3$)(NH$_2$NO$_2$), and B3: Ni(DNBTDO)(NH$_2$NO$_2$)$_2$]. Then, to check the probability of these six designed metal complexes as potential high-energy compounds, their molecular and electronic structures, heats of formation (HOFs), densities, energetic performance, initial decomposition mechanisms, sensitivity, infrared spectrums, and crystal structures were investigated systematically by using theoretical methods [including density functional theory (DFT), electrostatic potential data, and molecular mechanics (MM) methods], our main purpose is to investigate whether DNBTDO is an appropriate ligand in designing advanced energetic metal complexes. Since the energetic metal complex is the basis of HE-MOFs, if DNBTDO is a suitable ligand used for construct energetic metal complexes, it may also be appropriate to use in designing HE-MOFs.
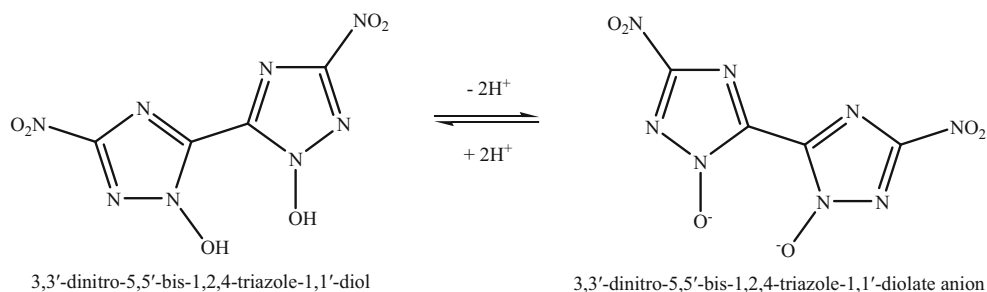
Computational methods

Molecular and electronic structures calculations of A1-A3 and B1-B3 were performed with the Gaussian program [12] by using generalized gradient approximation functional TPSS (Tao–Perdew–Staroverov–Scuseria) [13–15] at TPSSTPSS/6-311G(d,p) level. This method has been found to accurately calculate the structure of metal complexes [13–17].

The HOFs in solid phase were calculated by employing the atomization method:

$$\Delta_a H(0\ \mathrm{K}) = E(0\ \mathrm{K})[aC + bH + cN + dO + eM] - E(0\ \mathrm{K})[C_aH_bN_cO_dM_e] \quad (1)$$

$$\Delta_f H(0\ \mathrm{K})[C_aH_bN_cO_dM_e] = [a\Delta_f H(0\ \mathrm{K, C}) + b\Delta_f H(0\ \mathrm{K, H}) + c\Delta_f H(0\ \mathrm{K, N}) \quad (2)$$
$$+ d\Delta_f H(0\ \mathrm{K, O}) + e\Delta_f H(0\ \mathrm{K, M})] - \Delta_a H(0\ \mathrm{K})[C_aH_bN_cO_dM_e]$$

Fig. 1 DNBTDO in equilibrium with protonated and deprotonated states

3,3′-dinitro-5,5′-bis-1,2,4-triazole-1,1′-diol

3,3′-dinitro-5,5′-bis-1,2,4-triazole-1,1′-diolate anion

$$\Delta_f H(298\ K)[C_aH_bN_cO_dM_e] = \Delta_f H(0\ K)[C_aH_bN_cO_dM_e] + \Delta_c H[C_aH_bN_cO_dM_e]$$

$$- \left[a\Delta_c HC + b/2\Delta_c HH_2 + c/2\Delta_c HN_2 + d/2\Delta_c HO_2 + e\Delta_c HM \right] \tag{3}$$

where a, b, c, d, and e are the stoichiometric coefficients, M is metal atoms (Cu/Ni), E is the total energy of atoms at 0 K, $\Delta_a H$ is the heat of atomization at 0 K (the energy needed to atomize the constituent atoms in the compound into the most stable state), $\Delta_f H$ is the HOF and these of atoms and small molecules are taken from NIST database [18], $\Delta_c H$ is the enthalpy correction from 0 to 298 K. These above were calculated at TPSSTPSS/6-311G(d,p) level.

The detonation performance D and P of designed compounds were estimated by an advanced method [19] based on the Kamlet–Jacobs equations. The metal atoms are included and considered in this modified K-J equation and mean absolute values (MAVs) of relative deviation are less than 5%:

$$D = 1.01 \left(N\overline{M}^{1/2} Q^{1/2} \right)^{1/2} (1 + 1.30\rho) \tag{4}$$
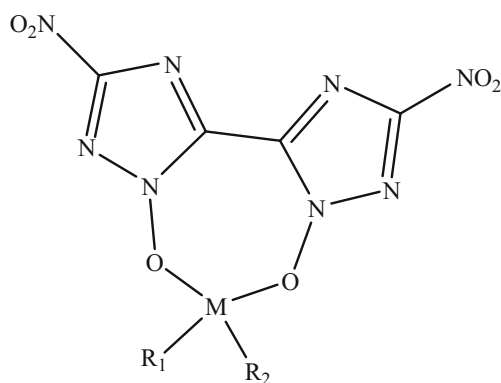
A1: M=Cu, R_1=R_2=NH$_3$
A2: M=Cu, R_1=NH$_3$ R_2=NH$_2$NO$_2$
A3: M=Cu, R_1=R_2=NH$_2$NO$_2$
B1: M=Ni, R_1=R_2=NH$_3$
B2: M=Ni, R_1=NH$_3$ R_2=NH$_2$NO$_2$
B3: M=Ni, R_1=R_2=NH$_2$NO$_2$

Fig. 2 Molecular frameworks of two series of designed compounds

$$P = 1.558\rho^2 N\overline{M}^{1/2} Q^{1/2} \tag{5}$$

where D is the detonation velocity, P is the detonation pressure, N is the moles of detonation gases per gram of explosive; $\overline{M}$ is the average molecular weight of these gases; Q is the heat of detonation; ρ is the density in solid phase, which was calculated by employing the electrostatic potential (ESP) method proposed by Politzer et al. [20] at B3PW91/6-31G(d,p) level:

$$\rho = \alpha \left(\frac{M}{V(0.001)} \right) + \beta\nu\left(\sigma_{tot}^2\right) + \gamma \tag{6}$$

where V(0.001) is the volume of the 0.001 electrons·bohr^{-3} contour of electronic density of the molecule, M is the molecular mass. The coefficients α, β, and γ are 0.9183, 0.0028, and 0.0443, respectively.

Natural bond orbital (NBO) analysis was carried out to identify the weaker bonds in designed metal complexes. Based on the NBO analysis, the bond dissociation energies (BDE) of relatively weaker bonds were calculated to compare thermal stability: $BDE(C–D) = E(C\cdot) + E(D\cdot) - E(C–D)$. The impact sensitivity (the degree to which an explosive can be initiated by impact, h_{50}, cm) was predicted by the ESP method [21] at B3PW91/6-31G(d,p) level:

$$h_{50} = a\sigma_+^2 + b\nu + c \tag{7}$$

where σ_+ is the electrostatic potential for the positive charge; ν is the degree of balance between the positive and negative potentials on an isosurface determined at 0.002 electron/bohr^3. The coefficients a, b, and c are the regression coefficients, which are −0.0064, 241.42, and −3.43, respectively.

Results and discussion

Geometric structures

Figure 3 displays the optimized structures of the designed compounds. It can be seen that DNBTDO acts as the bidentate ligand in all molecules and the triazole rings in all six metal

Fig. 3 Optimized structures of designed compounds
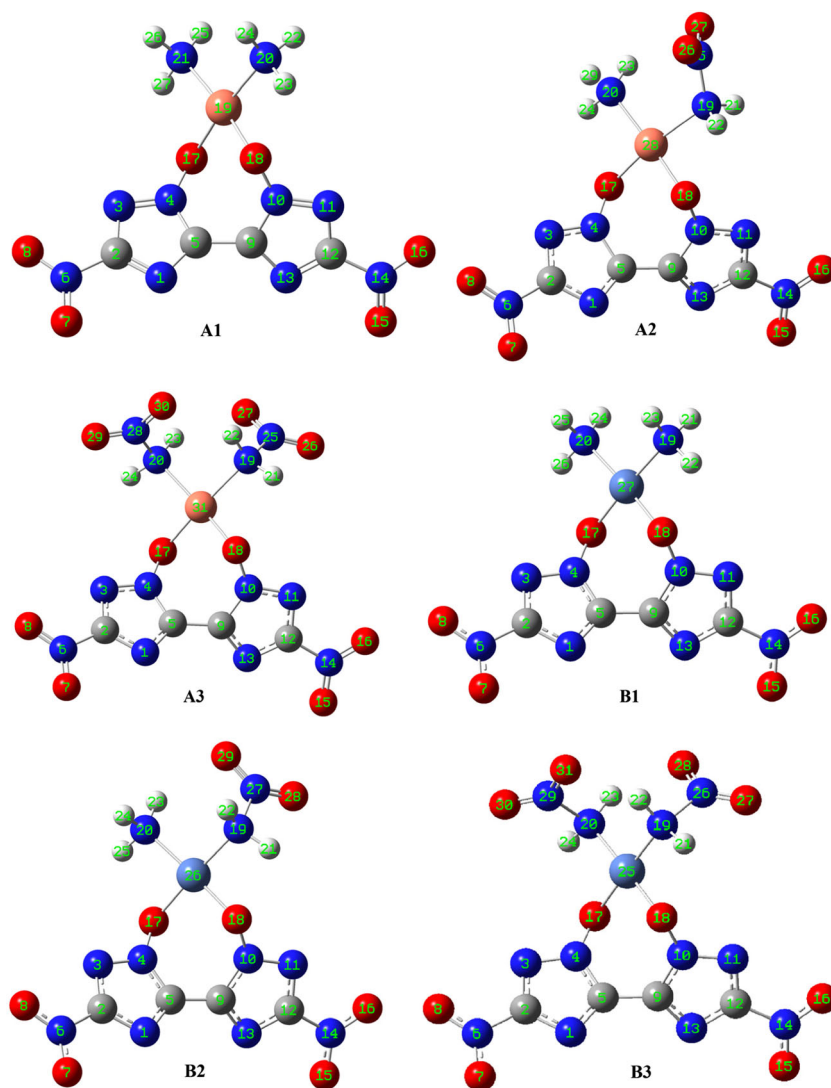
complexes are maintained. A new big seven-membered ring including two O atoms, two N atoms, two C atoms, and one metal atom (Cu or Ni) formed in both A1-A3 and B1-B3. Table 1 lists selected bond lengths for designed complexes. First, for A1 (R1 = R2 = NH$_3$), it is found that the same type bonds have the same bond length. For example, the five bonds in two triazole rings have just the same length ($L_{N1-C2} = L_{N13-C12}$, $L_{C2-N3} = L_{C12-N11}$, $L_{N3-N4} = L_{N11-N10}$, $L_{N4-C5} = L_{N10-C9}$, $L_{C5-N1} = L_{C9-N13}$), the bond lengths of two C-NO$_2$, Cu-O, Cu-NH$_3$ and N-OCu (N4-O17 and N10-O18 bonds) bonds are also the same, respectively. Similar phenomenon could be observed in A2-A3 and B1-B3, indicating the good symmetry of the structures of two series of designed metal complexes. This can be further supported by the fact that charges of these corresponding atoms are almost the same, respectively, such as O17/O18 atoms, there charges are −0.565/−0.565, −0.550/−0.549, −0.544/−0.544, −0.552/−0.552, −0.553/−0.557, −0.538/−0.538 for A1-A3 and B1-B3, respectively. Second, the bond lengths of two C-NO$_2$ bonds increase gradually

when energetic ligand NH$_3$ was replaced by NH$_2$NO$_2$, while metal atoms (Cu/Ni) have few effects on this. The lengths of N-OM (M = Cu/Ni) were not sensitive to both energetic ligands (NH$_3$/NH$_2$NO$_2$) and metal atoms, but those of M-O (M = Cu/Ni) decreases obviously when NH$_3$ was replaced by NH$_2$NO$_2$ or Cu was replaced by Ni. Then, B1-B3 have obviously shorter M-R bonds than A1-A3, which is just the opposite to previous work [17], in which the bidentate ligand is BTA (bistetrazoleamine). Finally, A2-A3 have shorter NH$_2$-NO$_2$ bonds than B2-B3, while NH$_2$-NO$_2$ bonds are one kind of key and sensitive bond for energetic materials, suggesting that metal atoms could affect the sensitivity of energetic metal complexes.

Detonation performance

Since most of the synthesized energetic metal complexes or MOFs possess lower detonation performance than existed widely used CHNO high explosives, it is thus important to find

Table 1 Calculated bond lengths (Å) for designed molecules

|	A1	A2	A3	B1	B2	B3
N1-C2	1.349	1.352	1.352	1.350	1.352	1.353
C2-N3	1.338	1.336	1.335	1.338	1.337	1.336
N3-N4	1.347	1.348	1.348	1.344	1.345	1.345
N4-C5	1.379	1.382	1.381	1.375	1.375	1.376
C5-N1	1.333	1.331	1.330	1.332	1.331	1.329
C5-C9	1.454	1.455	1.455	1.454	1.454	1.454
C9-N10	1.379	1.377	1.381	1.375	1.376	1.376
N10-N11	1.347	1.347	1.348	1.344	1.344	1.345
N11-C12	1.338	1.338	1.335	1.338	1.337	1.336
C12-N13	1.349	1.350	1.352	1.350	1.351	1.353
N13-C9	1.333	1.333	1.330	1.332	1.331	1.329
C2-NO_2	1.468	1.470	1.471	1.468	1.470	1.471
C12-NO_2	1.468	1.470	1.471	1.468	1.470	1.471
N4-O17	1.333	1.330	1.332	1.345	1.344	1.344
N10-O18	1.333	1.337	1.332	1.345	1.346	1.344
Cu/Ni-O17	1.922	1.925	1.906	1.843	1.839	1.839
Cu/Ni-O18	1.922	1.902	1.906	1.843	1.845	1.839
Cu/Ni-NH_3	2.033,2.033	2.004	/	1.935,1.935	1.935	/
Cu/Ni-NH_2NO_2	/	2.076	2.044,2.044	/	1.915	1.908,1.908
NH_2-NO_2	/	1.484	1.502,1.502	/	1.547	1.572,1.572

new high-energy MOFs that have comparative or even higher energy levels than these CHNO explosives [22, 23], like RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), or even CL-20 (hexanitrohexaazaisowurtzitane, which has highest energy in all synthesized CHNO energetic materials). Table 2 lists several important parameters [HOF, ρ (density), D, P, ΔH_{det}, OB] of detonation performance for designed molecules. It can be found that, first, the OB of six designed molecules are negative (−27.6% to −5.42%) but obviously higher than most of the synthesized energetic metal complexes and MOFs and comparable or better than RDX (−21.6%), HMX (−21.6%), and CL-20 (−10.5%). Then, it is seen that HOF, D, P, ΔH_{det} and OB all increase with the order of A1/B1, A2/B2, and A3/B3, indicating that NH_2NO_2 ligands are helpful in improving the detonation performance. Then, B1 and B2 have higher HOF, D, P, and ΔH_{det} than A1 and A2, respectively, showing that metal atoms also have greatly effects on the energetic metal complexes, and Ni is more useful in improving the energy including HOF and detonation performance than Cu in general. Besides, both A1-A3 and B1-B3 have obviously higher energy levels than the corresponding BTA-based complexes [17], showing the great effects of energetic ligands on detonation performance. However, it is interesting to find that B3 has lower energy than A3, indicating that the influence of metal atoms on the detonation performance is coupled with energetic ligands. Finally, all two series of designed molecules have extreme high densities more of than 2.2 g/cm^3 (2.22–2.26 g/cm^3), which results from the cooperative effect of metal atoms, the bidentate ligand, and small ligands. In addition, series B have higher densities than the corresponding BTA-based Ni complexes [17], which shows the effects of bidentate ligand on the density of energetic metal complexes. In all, since designed molecules have high density and positive HOF, they are expected to have

Table 2 Detonation performance of designed molecules

	A1	A2	A3	B1	B2	B3	RDX	HMX	CL-20
ρ (g/cm^3)	2.26	2.23	2.25	2.23	2.26	2.22	1.82	1.91	2.04
OB (%)	−27.2	−14.1	−5.42	−27.6	−14.3	−5.48	−21.6	−21.6	−10.5
HOF (kJ/mol)	130.2	190.1	266.8	150.8	213.9	280.7	93	460	105
ΔH_{det} (kcal/g)	0.88	1.35	1.49	1.17	1.34	1.48	1.44	1.32	1.55
D (km/s)	7.79	8.82	9.67	8.36	8.94	9.59	8.75	9.10	9.38
P (GPa)	30.5	38.9	46.9	34.9	40.2	45.8	34.5	39.0	44.6
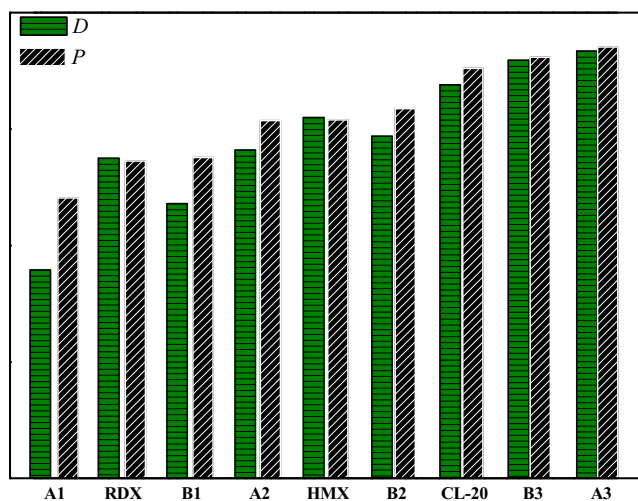
Fig. 4 A comparison of *D* and *P* of designed molecules, RDX, HMX, and CL-20

high detonation performance. Figure 4 displays a comparison of *D* and *P* of them with those of RDX, HMX, and CL-20. It is seen that B1 has comparative energy with RDX, A2 and B2 have comparable energetic performance to HMX, while A3 and B3 even have higher detonation properties than CL-20. This shows that the designed molecules have high detonation performance, especially for A3 and B3, which have *D* about 9.6 km/s and *P* about 46.0 GPa.

Stability and sensitivity

In this section, bond order (BO), BDE, and h_{50} were calculated to compare and judge the stability and sensitivity of designed molecules, respectively. It should be noted that the stability and sensitivity of energetic materials could be effected by many factors. BO, BDE, and h_{50} are three methods to estimate these. First, the BO of designed molecules was calculated, generally, the higher the BO is, the stronger the bond. It is found that M-O (M = Cu/Ni), M-R (M = Cu/Ni), C-NO$_2$, and N-NO$_2$ bonds have relatively lower BO among all kinds of bonds, as listed in Table 3. The BO of all M-O (M = Cu/Ni) and M-R (M = Cu/Ni) bonds ranged from 0.18–0.41, showing that these bonds are both ionic and covalent in nature. For all designed molecules, the M-O (M = Cu/Ni) bonds have obviously higher BO than M-R (M = Cu/Ni), indicating that the later bonds are weaker than

the former one. A2 has lower BO of NH$_2$-NO$_2$ bonds than A3, suggesting that this bond is more sensitive in A3, the same for B3 when compared to B2. The BO of C-NO$_2$ bonds are few influenced by ligands and metal atoms, since all designed molecules have close values.

Based on the NBO analysis, the BDE of M-R (M = Cu/Ni), C-NO$_2$ and N-NO$_2$ bonds were estimated and listed in Table 4. First, for A1 and B1, the Cu/Ni-NH$_3$ bond has the lowest BDE value, while this is the Cu/Ni-NH$_2$NO$_2$ of A2 and A3, suggesting that the Cu/Ni-NH$_3$ bond breaking and Cu/Ni-NH$_2$NO$_2$ bond breaking are the possible initial decomposition mechanism for A1/B1 and A2/A3, respectively. However, for B2 and B3, Ni-NH$_2$NO$_2$ bonds and N-NO$_2$ bonds have very close BDE values, indicating that both the Ni-NH$_2$NO$_2$ bond and N-NO$_2$ bond breaking may be the initiation decomposition mechanism. Then, the lowest BDE value of B1-B3 is obviously higher than A1-A3, showing that series B (Ni-based) has better stability than series A (Cu-based), and thus it may be inferred that metal atoms could affect the stability of energetic metal complexes, and the Ni atom is more helpful in improving the stability of DNBTDO-based metal complexes. Besides, it is interesting to find that these results are just the opposite to the case when the big bidentate ligand is BTA [17], indicating that the stability of metal complexes are dependent on both metal atoms and ligands. Finally, all designed molecules have obvious BDE values more than 20 kcal/mol [24] (about 83 kJ/mol, a criterion for chemical bonds could be thermal stable at room or even high temperature), suggesting that all designed molecules have acceptable stability, especially for B1. Figure 5 could provide further support for this, which displays the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of designed molecules, in which it can be seen that most of the atoms contribute to the HOMO or the LUMO, indicating that designed complexes are big conjugated systems that are helpful in enhancing the stability.

It was reported that the average absolute deviation of predicted results using the ESP method [21] from experiment values is 3 cm for 20 famous high explosives including RDX [25] (24–28 and 33 cm for experimental and predicted values, respectively) and HMX [25] (26–32 and 27 cm for experimental and predicted values, respectively). Thus, based on the ESP method, the impact sensitivity (h_{50}) of designed molecules was calculated and listed in Table 4. It can be seen

Table 3 Bond orders of designed molecules	A1	A2	A3	B1	B2	B3
Cu/Ni-O	0.229	0.237,0.240	0.247	0.383	0.385,0.411	0.410
Cu/Ni-NH$_3$	0.183	0.201	/	0.305	0.312	/
Cu/Ni-NH$_2$NO$_2$	/	0.150	0.166	/	0.283	0.298
NH$_2$-NO$_2$	/	0.889	0.873	/	0.829	0.805
C-NO$_2$	0.909	0.906	0.904	0.909	0.906	0.905

Table 4 BDE and h_{50} of designed molecules

| BDE (kJ/mol)	A1	A2	A3	B1	B2	B3
Cu/Ni-NH$_3$	147.8	171.0	/	194.5	209.4	/
Cu/Ni-NH$_2$NO$_2$	/	96.0	101.0	/	138.0	148.3
NH$_2$-NO$_2$	/	143.8	131.3	/	142.2	147.9
C-NO$_2$	275.6	267.0	268.3	327.9	313.3	269.3
h_{50} (cm)	25	22	23	24	24	27

that the h_{50} values of designed energetic metal complexes are in the range of 22–27 cm, which are comparative to RDX and HMX and higher than CL-20 (14 cm) [26], showing that the sensitivity of designed molecules is comparable with RDX and HMX but lower than CL-20. But it should be noted that RDX, HMX, and CL-20 are all belong to the group of sensitive explosives, thus, the designed complexes are also sensitive energetic materials, and researchers must be very careful when synthesizing or handling them. In addition, it was reported [27] that the ESP is related to the impact sensitivity of energetic molecules, which could be presented as a function of the imbalance between positive and negative regions, as shown in Fig. 6. First, it can be seen that in the center metal atoms, both the negative and positive ESP spatial regions are much weaker than that of other regions, suggesting that the

initiation decomposition locations may be bonds linked with metal atoms (Cu/Ni) directly. Then, the strong positive potentials are concentrated on the N atoms, indicating that these domains may also be the initial decomposition place. These two conclusion are in agreement with those of BDE above. Finally, the region of negative potential of the designed molecules is larger than that of positive potential, which is just the opposite to the case of many organic energetic materials and further shows the high energy of the designed molecules.

In all, A3 Cu(DNBTDO)(NH$_2$NO$_2$)$_2$ and B3 Ni(DNBTDO)(NH$_2$NO$_2$)$_2$ have better detonation properties and lower sensitivity than CL-20, A2 and B2 have comparable energetic performance and sensitivity to HMX, B1 has comparative energy level and sensitivity to RDX. These five energetic metal complexes may be potential HEDMs and attractive to energetic materials researchers.

Predicted crystal properties

In this section, we turn to predicting the crystal packing of designed molecules by the MM method (the molecular mechanics is a method which uses classical mechanics to model molecular systems, and the potential energy of all systems in molecular mechanics is calculated using force fields) using the Dreiding force field [27–29]. Table 5 lists the predicted

Fig. 5 The HOMO and LUMO of designed molecules
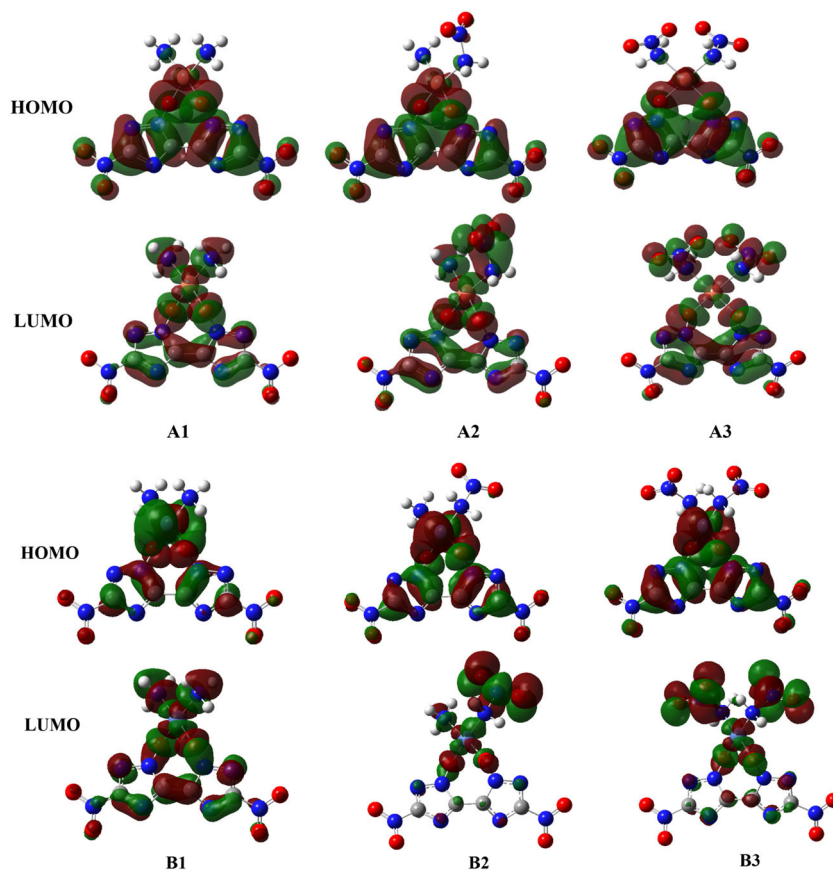
Fig. 6 The ESP of designed molecules [0.001 eletron·bohr^{-3} isosurface, color coding: from *red* (negative) to *blue* (positive)]
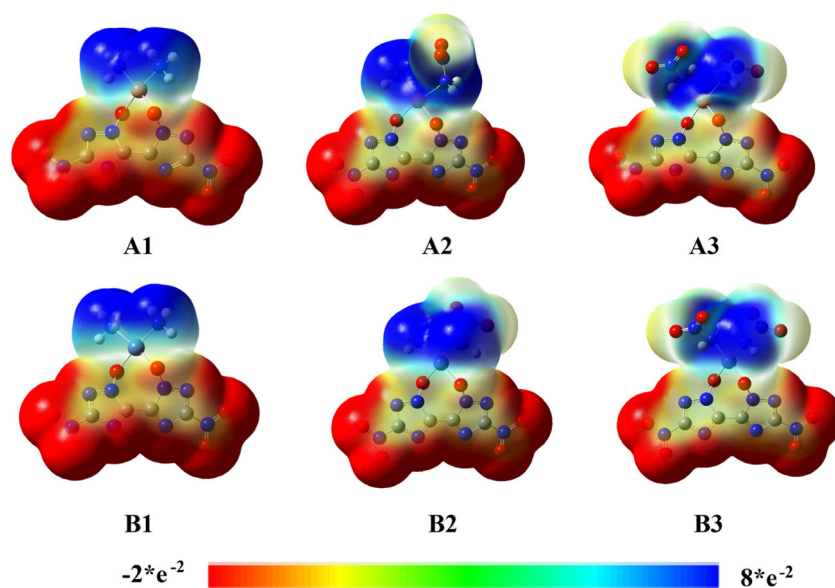
results. It can be seen that the structure of A1, A3, B2 and A2, B1, B3 with $P2_1$/c symmetry P-1 symmetry has the lowest energy among all ten results, respectively. In general, the lower the total energy is, the more stable the polymorph. Thus, it may be deduced that A1, A3, B2 and A2, B1, B3 most probably belong to the $P2_1$/c and P-1 space group, respectively. Thus, the lattice parameters of A1, A2, A3, B1, B2, and B3 are predicted to be a = (14.23, 11.38, 17.84, 11.30, 18.05, and 10.55 Å), b = (16.20, 8.79, 9.37, 29.94, 14.29, and 14.91 Å), c = (9.17, 8.88, 15.25, 7.74, 23.28, and 6.81 Å), α = (90.0°, 65.2°, 90.0°, 119.6°, 90.0°, 92.0°), β = (142.8°, 61.8°, 37.4°, 117.5°, 166.4° and 71.2°) and γ = (90.0°, 77.5°, 90.0°, 16.1°, 90.0° and 130.2°), respectively.

Conclusions

In the present work, using a high OB high-energy compound DNBTDO as the bidentate ligand, NH_3 and NH_2NO_2 as short energetic ligands, and Cu/Ni as the metal atoms, two series of novel energetic metal complexes were computationally designed. Their molecular and electronic structures, and properties including HOF, energetic performance, decomposition mechanism, stability, and sensitivity were studied systematically by DFT and MM methods. The results showed that the designed metal complexes are a big conjugated system and have good symmetry in structures, making them have acceptable stability and sensitivity used as high-energy materials. Both the energetic ligands and metal atoms could have a great influence on the structures, HOF, detonation properties, and stability of energetic metal complexes, and the effects are coupled with each other. All designed molecules have positive HOF, extremely high density, and relatively high OB, making most of them have high energy levels. B1 has comparative energy with RDX, A2 and B2 have comparable energetic performance to HMX, while A3 and B3 even have higher detonation properties than CL-20. The analysis of BDE and ESP both indicate that Cu/Ni-R and NH_2-NO_2 bond breaking are two possible initial decomposition mechanisms for designed complexes. In a word, several new high OB energetic metal complexes with good overall performance were designed and obtained successfully by using DNBTDO as the big bidentate energetic ligand; among them, A3 and B3 have better detonation properties and lower sensitivity than CL-20, A2 and B2 have comparable energetic performance and sensitivity with HMX, B1 has comparative energy level and sensitivity with RDX. These five

Table 5 Total energy (kJ/mol/cell) of designed molecules in the ten possible space groups

	$P2_1$/c	P-1	$P2_12_12_1$	Pbca	C2/c	$P2_1$	Pna2$_1$	C2	CC	Pbcn
A1	−9.279	−9.167	−7.583	−7.969	−8.888	−8.015	−8.021	−7.266	−8.600	−7.610
A2	−8.444	-8.542	−7.463	−7.596	−8.406	−7.364	−8.193	−6.972	−7.493	6.695
A3	-7.731	−7.508	−6.133	−6.341	−7.227	−7.280	−6.417	−6.006	−6.680	−5.796
B1	3.719	3.326	3.740	4.094	3.799	4.005	3.827	3.487	3.441	4.797
B2	4.680	5.550	6.572	6.081	5.859	5.939	6.232	5.897	6.144	6.414
B3	7.502	6.464	8.759	8.350	7.367	8.397	8.776	8.503	7.629	8.510

energetic metal complexes may be potential HEDMs and attractive to energetic materials researchers. However, it should be noted that these novel metal complexes belong to the group of sensitive explosives, and the synthesis risk and difficulty may be high. In all, DNBTDO is a suitable ligand used for obtaining advanced energetic metal complexes and may also be appropriately used for designing new HE-MOFs.

Compliance with ethical standards

Conflict of interest The authors declare no competing financial interests.

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