

Theoretical studies on BTA-Metal (M=Ni, Cu) Complexes as High Energy Materials

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Abstract. Metal complexes of Nickel and Copper with the dianion of bidentate chelating agent BTA [N,N-bis(1(2)H-tetrazole-5-yl)-amine] along with NH_3 and NH_2NO_2 ligands were designed. A total of four metal complexes having the compositions such as $\text{M}(\text{BTA})(\text{NH}_3)(\text{NH}_2\text{NO}_2)$ and $\text{M}(\text{BTA})(\text{NH}_2\text{NO}_2)_2$ where M is the metal atom, were formulated and subjected to detailed theoretical study to explore their energetic properties. Density Functional Theory (DFT) was used to predict the optimized geometry of the complexes at TPSS/6-311G(d,p) level. The heats of formation of the metal complexes were determined using atomization method. Crystal densities of the salts were predicted using the data obtained at B3PW91/6-31G(d,p) level utilizing the wave function analysis (WFA) program. Results indicate that all the designed compounds possess density in the range of $2.18\text{--}2.25\text{ g cm}^{-3}$. This is the remarkable feature of the title compounds because loading density is one of the desired properties for increasing the detonation performance of energetic materials. The calculated impact sensitivities ($h_{50, \text{cm}}$) show that the three of the designed compounds are comfortably insensitive towards impact ($h_{50, \text{cm}} \sim 42$) in comparison to the experimentally determined values for the commercially used powerful explosives such as RDX (24–28 cm) and HMX (26–32 cm). $\text{Ni}(\text{BTA})(\text{NH}_2\text{NO}_2)_2$, the fourth designed compound has a value almost similar to that of RDX and HMX. The calculated detonation parameters D (detonation velocity) and P (detonation pressure) are predicted to be in the range of $7.7\text{--}8.5\text{ km s}^{-1}$ and $29.5\text{--}36.1\text{ GPa}$, respectively. Results obtained in the present study predict that the designed compounds can be used as high energy density materials (HEDs).

Keywords. DFT; metal complexes; impact sensitivity; BDE.

1. Introduction

Increasing demand of high energy materials due to their utility in a wide variety of applications has drawn considerable attention of theoretical and synthetic chemists in designing and synthesis of new and advanced high energy density materials (HEDMs).^{1–5} New strategies have been adopted for increasing the density and energetics of such materials. Recently, Mondal *et al.*,⁶ have adopted such an approach using computational methods to design C H N O based energetic materials which were found to possess considerably high performance values. Molecular species rich in nitrogen content play an important role in the development of new energetic materials.^{7–11} Nitrogen rich ligands have also been found to form a variety of metal-organic frameworks (MOFs) that have found wide applications such as gas storage,¹² and industrial applications.^{13,14} Such MOFs have attained focused attention in view of their applications as high energy materials.^{15,16} The high heats of

formation of nitrogen-rich compounds are associated with the presence of a considerable number of inherent energetic N–N, N=N, C=N, C–N, N=O and N–O bonds. The high energy associated with such molecules may be ascribed to the fact that the elemental nitrogen present in such molecules comes out in the form of molecular nitrogen, N_2 whose bond enthalpy is about 954 kJ/mol .¹⁷ In contrast to the traditional energetic materials, such as TNT (2,4,6-trinitrotoluene), RDX (1,3,5-trinitro-1,3,5-triazinane), and HMX (1,3,5,7-tetra-nitro-1,3,5,7-tetrazocane) whose energies are derived mostly from the oxidation of the carbon backbone by oxygen present in the molecule and the energy associated with the ring or cage strain, the detonation energy in the nitrogen rich compounds are derived from the inherent energy associated with N–N and C–N bonds. Unfortunately, many energetic materials with high performance values exhibit high sensitivities toward physical stimuli and the materials with the desired sensitivity lack the high performance. Therefore, the investigation of new energetic materials with higher performance and lower sensitivity is the need of modern weaponry and

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industrial applications that warrants a serious effort to search for new high energy density materials (HEDMs). Transition metal complexes with nitrogen-rich ligands have attracted considerable interest due to their high N-content, good thermal stability and preferred energetic properties.^{1,18} These complexes provide a new insight for the development of safe and high performance energetic materials. N,N-bis(1(2)H-tetrazol-5-yl)-amine (H₂BTA) is one of the promising green energetic materials with a high nitrogen content (N% = 82.4). A number of energetic ionic salts and ionic liquids based on H₂BTA have been investigated.^{19–23} Interestingly, protonated and deprotonated forms of H₂BTA exist in a reversible manner as shown in Figure 1 and works as an effective ligand in devising nitrogen rich energetic materials.

BTA is a bidentate chelating ligand and such ligands are found to form stable complexes. In fact, it is suggested that by using BTA as a bridging ligand, the molecular architecture of the metal complex can be modified for varying physicochemical and explosive properties by suitably changing the outer- and inner-sphere ligands.¹⁸ BTA copper complexes with ammonia as ligand, Cu(BTA)(NH₃)₂, have been synthesized by Klapötke's group and have been found to be thermally stable (T_m 300–400°C).¹⁸ These complexes have been found to be quite insensitive to impact and friction (impact sensitivity > 40 J and friction sensitivity > 350 N) and detonation velocity (D) and detonation pressure (P) of 6.07 km/s and 17.32 GPa, respectively.²⁴ Tao *et al.*,²⁵ have synthesized nitrogen rich salts of Cu(II) and Cd(II) with 5,5'-azobistetrazolate which yielded D and P values as 8.23 km/s and 32.84 GPa, respectively.²⁴ In another study, Tao *et al.*,²⁶ used nitrogen rich 5-(1-methylhydrazinyl) tetrazole (MHT) ligand to synthesize copper and silver complexes, some of which had nitrogen content as high as 73.65%. These complexes have been found to possess high energy content and insensitive to impact (Impact Sensitivity > 40J).²⁶ Fe(III) complexes with highly rich nitrogen ligand have also been synthesized by Cook *et al.*²⁷ In addition to the above, Li *et al.*,¹ also reported several other energetic salts based on BTA.

Thus, we thought to make a detailed theoretical investigation of transition metal complexes of Ni and Cu

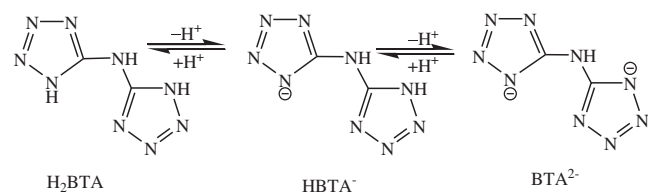


Figure 1. H₂BTA in equilibrium with protonated and deprotonated states.

using bidentate BTA dianion and nitramide (NH₂NO₂) as complexing agents and explore their energetic properties. Nitramide ligand was taken to replace the NH₃ ligand of Cu(BTA)(NH₃)₂ because NH₃ and NH₂NO₂ both possess N atoms which involve its lone pair electrons in binding it to the metal atom. BTA in its deprotonated form and ammonia and/or nitramide would provide more than half a dozen N atoms that can coordinate to central metal ion with versatile coordination modes.¹ The possibility of using nitramide (NH₂NO₂) is considered in view of the fact that nitro group is a well-known explosivesophore whereas the presence of amino group usually leads to stability. Thus, the use of nitramide ligand might provide a leverage in maintaining a compromise between brisance and stability.

In view of the above reports, mono- and dinitramide derivatives of metal-BTA complexes schematically shown in Figure 2 have been designed and subjected to detailed study.

The heats of formation of the designed compounds were determined using the atomization procedure which has been found to yield reliable estimates for N-rich compounds.^{4,5} In order to look into the possibility of using the designed compounds as high energy materials, crystal densities were determined using the method devised by Politzer *et al.*,²⁸ based on the electrostatic potential data obtained from WFA Program.²⁹ The detonation parameters, *viz.*, detonation velocity (D) and detonation pressure (P) were calculated using Kamlet-Jacobs equations.³⁰ The impact sensitivities of all the designed compounds were also estimated with the help of electrostatic potential data.

2. Computational

2.1 Electronic structure studies

Electronic structure calculations of the designed metal complexes were performed using generalized gradient approximation (meta-GGA) functional proposed by Tao-Perdew-Staroverov-Scuseria (TPSS)^{31–33} with 6-311G(d,p) basis set as implemented in the Gaussian09

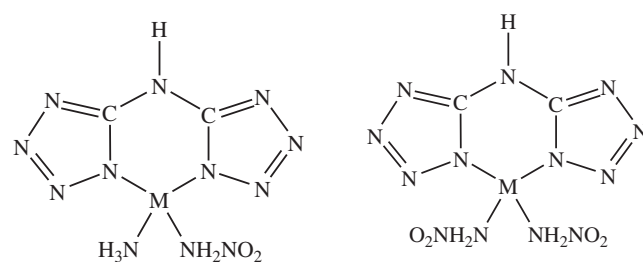


Figure 2. Schematic representation of the designed compounds. (M=Ni, Cu).

suite of program.³⁴ Extended basis set with polarized functions on lighter atoms was used to take into account the highly delocalized electrons of the designed molecules. TPSS functional has been found to predict reliable structural parameters in many metal complexes. Rydberg and Olsen³² studied iron porphyrin complexes with seven different functionals and concluded that TPSS functional yielded the best results (absolute bond distance deviations of 0.015–0.016 Å). Rayon *et al.*,³³ made computational studies on Zn(II) complexes using various functionals and also concluded that TPSS functional were the ones that performed the best. In studying the 2D polymeric complexes of Cu(II) and Zn(II), Shu *et al.*,³⁵ concluded that TPSS functional was a good choice for predicting the geometrical parameters of metal-complexes. The optimized structures of the designed metal complexes were subjected to vibrational frequency calculation in order to ascertain that the structure belonged to true minima on their respective potential energy surfaces. This was ascertained by the fact that all the calculated vibrational frequencies were positive and no imaginary frequency was present.

2.2 Heat of formation

The heats of formation of the designed molecules were calculated using the atomization procedure. This procedure has been widely used and found to yield reliable thermal data for nitro substituted energetic molecules.^{4,5,35} In the case of Cu(II) and Zn(II) complexes with diaminotetrazole (DAT) Shu *et al.*,³⁵ have shown that atomization method yielded reliable values of the heat of formation by performing calculations on DFT/TPSS/6-311++G(d,p)//TPSS/6-311G(d,p) level. The method is based on the scheme using Hess's law as shown in Figure 3. In this scheme, Step 1 is the heat of atomization ($\Delta_a H$) at 0 K of a species

stoichiometrically designated as $C_a H_b N_c O_d M_e$ and it is defined as the energy needed to atomize the constituent atoms present in the molecule into their most stable state represented as $C(^3P)$, $H(^2S)$, $N(^4S)$, $O(^3P)$, $Ni(^3F)$ and $Cu(^2D)$. The energy involved in Step 2 is the sum of the gas phase heats of formation of the elements in their most stable state suitably multiplied by their corresponding stoichiometric coefficients. The heat involved in Step 3 is the desired heat of formation. The details of the procedure involved in the determination of the heat of formation of the designed molecules are given in Supplementary Information (S1).

2.3 Detonation properties

The detonation parameters D (km/s) and P (GPa) are calculated using Kamlet-Jacobs equations given as follows:

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \quad (4)$$

$$P = 1.558\rho^2NM^{1/2}Q^{1/2} \quad (5)$$

where Q is the heat of detonation, ρ the loading density, N, the number of moles of detonation gases per gm of the explosive and M, the average molecular weight of the gaseous detonation products. The details of the method involved in the calculation of the heat of detonation, Q is given in the Supplementary Information (S2).

2.4 Density

For the designed molecules experimental value of density is not known therefore, theoretical procedures have been considered as a viable option. Loading density is a critical parameter on which the detonation parameters are strongly dependent. It can be represented in its simplest form as:

$$\rho = M/V_{m(0.001)} \quad (6)$$

where M is the molecular mass of the designed explosive in gm per molecule, and $V_{m(0.001)}$ is the molecular volume of an isolated gas phase molecule in cm^3 per molecule, determined at 0.001 electron/bohr³ density space. It was obtained by performing 100 single point energy calculations on the optimized structures of the molecules using Monte Carlo integration method as implemented in the Gaussian09 suit of program. Thus, the average volume was used for the calculation of the density using equation 6. However, the most important missing part while using the Monte Carlo integration method is that no allowance is made to take into account the specific intermolecular interaction taking

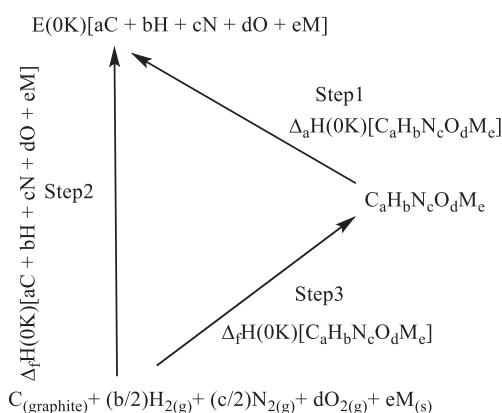


Figure 3. Thermodynamic cycle for the determination of heat of formation using atomization method.

place in the crystal lattice during its packing. Politzer *et al.*,²⁸ developed an improved method for determining the crystal density by considering the role played by the intermolecular forces in the crystal lattice and provided an expression for determining the crystal density using electrostatic potential data, as shown below.

$$\text{Crystal density}(\rho) = \alpha(M/V_{m(0.001)}) + \beta(\nu\sigma_{\text{total}}^2) + \gamma \quad (7)$$

where α , β , and γ are empirical parameters and ν and σ_{total}^2 are the balance parameter and total variance which are related to electrostatic potentials due to positive and negative charges as follows:

$$\nu = \frac{\sigma_+^2\sigma_-^2}{\sigma_{\text{total}}^2} \quad (8)$$

$$\sigma_{\text{total}}^2 = \sigma_+^2 + \sigma_-^2 \quad (9)$$

In the above expressions, σ_+ and σ_- are the electrostatic surface potentials due to positive and negative charges in the molecule. The square of these potentials were taken to make them positive. σ_+^2 , σ_-^2 and σ_{total}^2 are measures of the strength and variabilities of the positive, negative and total surface potentials. The degree of balance between the positive and negative surface potentials on the isosurface is measured by ν . $\nu\sigma_{\text{total}}^2$ is a measure of the variability of the electrostatic potential on the molecular surface and it has been shown to be an important parameter in relating macroscopic properties that are dependent on non-covalent electrostatic interactions. They determined the values of empirical parameters α , β , γ by performing calculations at B3PW91/6-31G(d,p) level for a set of trainee molecules. They fitted the experimental and calculated densities using equation 7 and listed the fitting parameters α , β , and γ to be 0.9183, 0.0028, and 0.0443, respectively. In order to use the values of parametric constants α , β , and γ as listed by Politzer *et al.*,²⁸ we also utilized the same level of theory, for the geometry optimization of all the designed metal complexes. These optimized structures were utilized to evaluate the value of $V_{m(0.001)}$. These structures were also used to calculate the values of ν and σ_{total}^2 utilizing the electrostatic potential (ESP) method with WFA-SAS code.²⁹ The electrostatic parameters needed during the estimation of density using equation 7 are given in the Supplementary Information (Table S1 in Supplementary Information).

2.5 Impact sensitivity

The term 'sensitivity' refers to the ease with which the initiation of reaction in an energetic material is achieved. This leads to self-decomposition process

yielding high temperature and pressure and ultimately to explosion. In more specific terms, it refers to the vulnerability of the energetic compound when the latter is subjected to external stimuli such as impact, shock, heat, friction, and spark. Impact sensitivity is commonly measured by the height from which a mass 'm' dropped on the compound produces detonation 50% of the time. The sensitivity is then expressed as either the drop height, h_{50} (usually in cm) or as impact energy mgh_{50} in joules. The larger the value of h_{50} , the lower is the sensitivity. For a 2.5 kg mass, the impact energy for a h_{50} of 100 cm would correspond to about 24.5 J. For known explosives, experimental tools are available and a statistical value of h_{50} can be determined. However, for designed molecules computational approach have been adopted. Pospíšil *et al.*,³⁶ have correlated the explosive characteristics of an energetic material to the electrostatic potential of the molecule, and proposed an empirical formula relating h_{50} to the electrostatic potential of the molecule as given by the following expression:

$$h_{50} = a\sigma_+^2 + b\nu + c \quad (10)$$

where σ_+ is the electrostatic potential for the positive charge and ν is the degree of balance between the positive and negative potentials on an isosurface determined at 0.002 electron/bohr³ of the energetic molecule. The coefficients a, b and c are the regression coefficients listed by Pospíšil *et al.*,³² as -0.0064, 241.42 and -3.43, respectively. In order to use these parametric constants, the calculation during the present study was also performed keeping the same level of theory as used by Pospíšil *et al.*³⁶ The electrostatic parameters needed for the calculation of h_{50} using equation 11 are given in Supplementary Information (Table S1).

2.6 Oxygen balance

A simple parameter such as oxygen balance cannot be depended upon to yield universally consistent results on sensitivity, brisance, and strength of complex explosive material. However, a simple relationship such as this can be used to predict the properties of one explosive relative to another. It is to be expected that one with an oxygen balance closer to zero would be preferred in terms of detonating power and brisance. However, many exceptions to this rule do exist. Oxygen balance, represented as Ω , is defined as the ratio of the oxygen content of the compound to the total oxygen required for the complete combustion of all the constituents present in the molecule. It is represented in terms of the percentage of oxygen required for complete conversion of carbon to carbon dioxide, hydrogen to water,

nitrogen to N₂, and any metal to its oxide. It is calculated as follows

$$\Omega = \frac{(O - 2C - \frac{H}{2} - xZ) \times 1600}{\text{Molecular mass of the compound}} \quad (11)$$

where O, C, H and Z are the number of oxygen, carbon, hydrogen and metal atoms. In the present case of Ni and Cu the value of x is taken to be unity.¹

3. Results and Discussion

3.1 Electronic structure studies

Electronic structure calculation of all the four designed complexes was performed at TPSS/6-311G(d,p) level. In order to see the reliability of the data predicted by TPSS functional, we performed calculation on Cu(BTA)(NH₃)₂, a compound which has been synthesized in the past and its structural parameters determined experimentally.¹⁸ The additional advantage in selecting this complex is that it is very much similar to the title complexes considered during the present investigation. Results of a few selected parameters of Cu(BTA)(NH₃)₂ are recorded in Table 1 which show a good agreement between the experimental and theoretical values. The geometry optimization and frequency calculation of all the designed complexes were made using TPSS functional and 6-311G(d,p) basis set. The geometry of the designed molecules in terms of their internal coordinates are given in the Supplementary Information (Tables S2–S5 in Supplementary Information). The absence of any imaginary frequency in the frequency calculation data showed that the optimized structures belong to minima on their corresponding potential energy surface.

The optimized structures of the title compounds along with the reference compound, Cu(BTA)(NH₃)₂ are shown in Figure 4. A detailed analysis of the

structures performed with the *Gaussview* visualization program³⁷ reveals that the structural features of the BTA ring in the metal complexes remain the same. The results listed on the optimized structures as shown in Figure 4 reveal that in the case of the designed Cu(II) complex, when one of NH₃ ligand is replaced by NH₂NO₂, the Cu–N bonds with BTA are slightly decreased (~1%) whereas the Cu–N bond with dinitramide ligand is slightly increased (~3%) in comparison to the Cu–N bonds with NH₃. This slight increase in the latter may be due to the fact that NO₂ group being an electron withdrawing group draws electrons from the N of the NH₂ resulting in a decrease in its electron density. This is corroborated by the NBO analysis and the results listed on the optimized structure records this decrease to be from 0.674 to 0.488. This decrease in electron density is probably responsible for the increase in the bond length. This would result in a weaker Cu–NH₂NO₂ bond. This conclusion is also in accord with the NBO analysis performed on Cu(BTA)(NH₃)(NH₂NO₂) which predicts a decrease in the corresponding bond order from 0.215 to 0.160. On the other hand, a slight decrease in the bond lengths of the Cu–N bonds with BTA dianion shows it to be strengthened because of the slight increase (from 0.631 to 0.641) in the electron density at the N atoms of BTA bonded to Cu. Additionally, an increase in the positive charge on Cu from 1.159 to 1.168 results in an increased electrostatic interaction resulting in a slight decrease of the bond lengths.

In the case, where both the NH₃ ligands of Cu(BTA)₂(NH₃)₂ are replaced by NH₂NO₂ ligand, both the Cu–N bonds with dinitramide ligands are found to be 2.043 Å whereas the Cu–N with BTA are 1.903 Å. The positive charge on the Cu atom in this case is calculated to be 1.173 which is slightly increased as compared to the mononitramide derivative. This may be due to the fact that there are almost equal charges (0.513

Table 1. A comparison of experimental and calculated values of selected parameters of Cu(BTA)(NH₃)₂. Refer to figure 4 for the atom numbers.

Bond distance (Å)		Bond Angle (°)	
N3–N4	1.376 (1.353)*	N4–Cu–N9	87.72 (85.55)
N8–N9	1.376 (1.359)	N4–Cu–N10	87.65 (91.70)
C11–N4	1.349 (1.345)	N4–Cu–N11	175.37 (154.83)
C12–N9	1.349 (1.330)	N9–Cu–N10	175.37 (176.74)
C11–N5	1.378 (1.362)	N9–Cu–N11	87.65 (91.32)
C12–N5	1.378 (1.369)	N10–Cu–N11	87.72 (91.91)
Cu–N4	1.929 (1.999)		
Cu–N9	1.929 (1.977)		
Cu–N10	2.041 (2.005)		
Cu–N6	2.041 (2.007)		

*Values given in brackets are experimental values taken from Ref. 18.

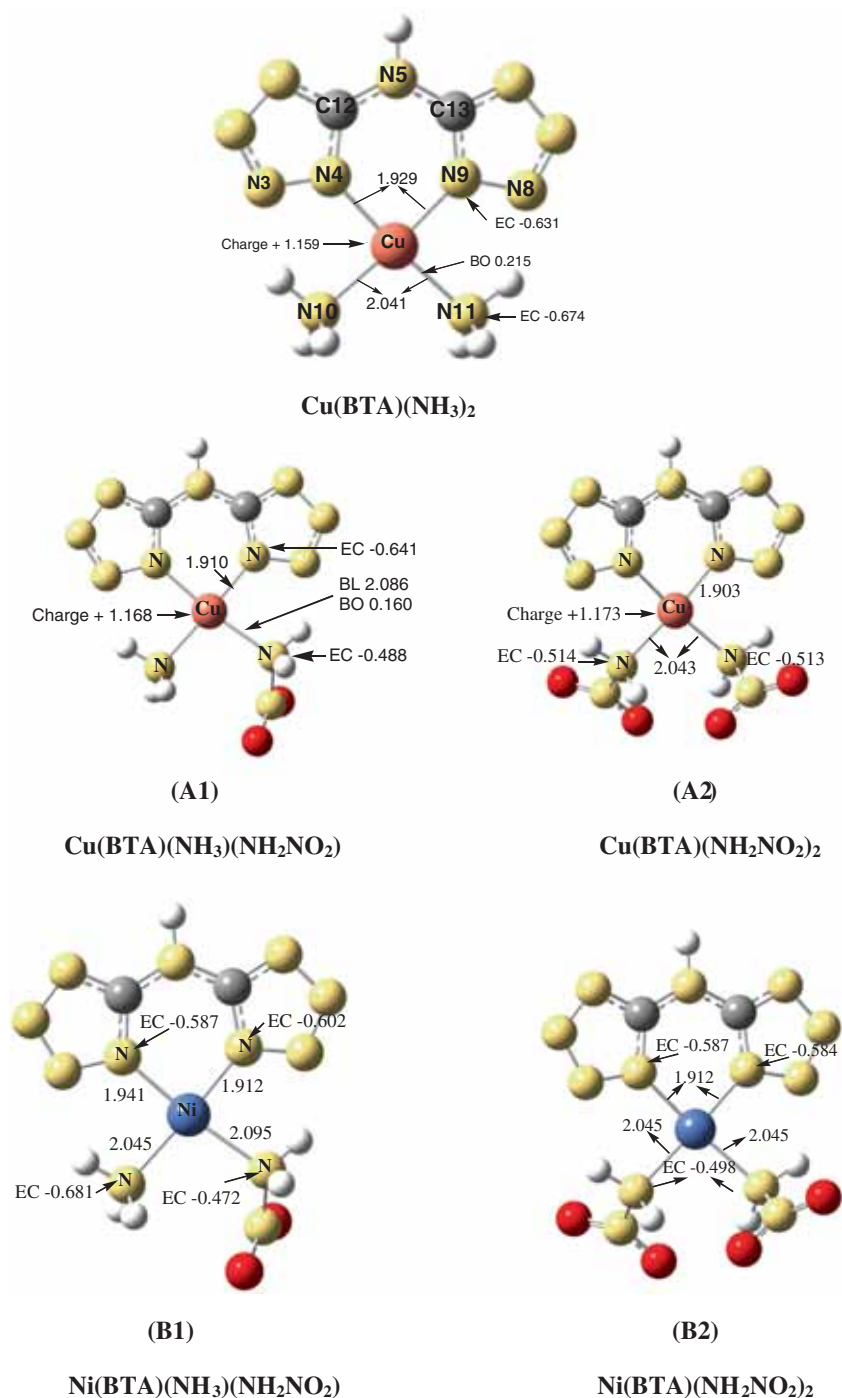


Figure 4. Optimized structures of the designed molecules. The acronyms EC, BO and BL refer to electronic charge, bond order and bond length, respectively.

and 0.514) on both of the nitrogen atoms of nitramide ligand bonded to Cu. The almost equal charges make both of the bond distances to be 2.043 Å. Detailed analysis of the optimized structure of this complex shows that Cu remains in the basal plane bonded with nitrogen atoms of BTA and NH₃ and/or NH₂NO₂. The same is also true in the case of Ni complexes where the Ni–N bonds with the BTA are 1.941 and 1.912 Å and Ni–NH₃

(2.045 Å) and Ni–NH₂NO₂ (2.095 Å) remain in the same range as that in the case of Cu. However, a detailed NBO analysis reveals that all the nitrogen atoms bonded to Ni have lower electron density as compared to their Cu(II) analogs as listed in Figure 4. This makes all the Ni–N bonds longer than their corresponding Cu–N bonds. This has been found to be true during the present study and the results are recorded along

the corresponding bonds in Figure 4. The same conclusion is drawn while analyzing the optimized structure of Ni(BTA)(NH₂NO₂)₂ complex and a few structural parameters are listed in Figure 4. Analysis of the structure with *Gaussview*³⁷ further reveals that Ni atom also remains in the basal plane with a slight variation in the case of the dinitramide derivative.

3.2 Decomposition mechanism

Bond dissociation energy (BDE) has been frequently used as a measure of the thermal stability of a compound.^{38,39} In the present study, thermal stabilities of the designed molecules have been investigated by calculating the bond dissociation energies (BDE) of various fragile bonds. The BDE is defined as the difference in the zero point corrected total energies at 0 K of the parent molecule and that of the product species formed during the unimolecular bond dissociation process. BDE of a few plausible breaking bonds that could act as a trigger linkage are calculated and the results are recorded in Table 2. The BDE of such bonds are also shown on the optimized structure of the compound given in Supplementary Information (Figure S1 in Supplementary Information). The free energy and entropy change along with the activation barrier associated with the respective dissociative channel considered to be a trigger linkage are also recorded in Table 2. All the dissociative channels are found to progress with a positive entropy change. This is reasonable because bond breaking processes lead to an increase in the number of the product species. However, the calculated value of the entropy changes (Table 2) for each of the dissociative channels is very small and therefore, it is inferred that all the processes are thermally driven. The calculated Gibb's free energy changes for all reactions considered are highly positive. This shows that the designed molecules are thermodynamically stable at room temperature. This is also in conformity with the observation made by Mondal *et al.*,⁶ that compounds having a BDE of 20 kcal/mol

(~80 kJ/mol) for the most fragile bond are thermally stable at room temperature or even at high temperature.

A close examination of the transition states reveals that each one of these states is more product-like having activation barrier slightly greater than the reaction enthalpy. This is in accord with the Hammond's postulate which states that endothermic processes progressed with a late transition barrier.⁴⁰ In the case of copper mononitramide complex, the Cu(NH₂)–NO₂ bond energy is calculated to be 130 kJ/mol which is much lower than the N–NO₂ bond energy of 230 kJ/mol⁴¹ in free NH₂NO₂. This may be due to the fact that the lone pair of electrons available with the N of the NH₂NO₂ is strongly involved in the bond making process with Cu. On the other hand, the Cu–NH₂NO₂ bond energy is found to be 109 kJ/mol. This shows that in the case of Cu(BTA)(NH₃)(NH₂NO₂) the Cu–NH₂NO₂ bond is the most fragile bond and it may work as a trigger linkage. The calculated barrier heights for the Cu–NH₂NO₂ and Cu(NH₂)–NO₂ bond breaking are found to be 112 and 126 kJ/mol. This shows that in the case of Cu-mononitramide BTA complex (**A1**), the Cu–NH₂NO₂ bond breaking process is kinetically more favourable as compared to Cu(NH₂)–NO₂ bond breaking.

In the case of the designed compound (**A2**) when both of the NH₃ ligands of Cu(BTA)(NH₃)₂ are replaced by NH₂NO₂, the Cu–NH₂NO₂ bond energy is calculated to be 165 kJ/mol whereas the N–NO₂ bond energy of the nitramide is lowered down to 119 kJ/mol. The increase in the bond strength of Cu–NH₂NO₂ in the case of dinitramide complex may be assigned to the fact that in such a case the molecule becomes more symmetrical and the N of both NH₂NO₂ ligands donate the electrons to the metal with the same strength. As a result, the N–NO₂ bond gets weaker and may act as a trigger linkage. The calculated barrier heights for these two bond breaking processes in **A2**, *viz.*, Cu–NH₂NO₂ and Cu(NH₂)–NO₂ are found to be 135 and 110 kJ/mol, respectively, as listed in Table 2. This also suggests that in the case of designed molecule **A2**, Cu(NH₂)–NO₂

Table 2. Bond dissociation energy, activation barrier, reaction free energy and entropy change of various bond breaking processes.

Molecule	Bond	BDE _{ZPE} (kJmol ⁻¹)	Activation barrier (kJmol ⁻¹)	Δ _r G ⁰ (kJmol ⁻¹)	Δ _r S ⁰ (Jmol ⁻¹ K ⁻¹)
A1	Cu–NH ₂ NO ₂	109	112	60.3	16.4
	Cu(NH ₂)–NO ₂	130	126	78.7	18.4
A2	Cu–H ₂ NO ₂	165	135	111	19.3
	Cu(NH ₂)–NO ₂	119	110	67.8	18.5
B1	Ni–NH ₂ NO ₂	103	104	55.2	15.9
	Ni(NH ₂)–NO ₂	107	104	56.1	18.5
B2	Ni–NH ₂ NO ₂	114	120	63.7	16.8
	Ni(NH ₂)–NO ₂	99	110	47.2	18.3

would act as a trigger linkage. The calculated values of BDE's and activation barriers for Ni complexes (**B1** and **B2**) as listed in Table 2 also suggest that these two complexes of Ni also follow the same trend.

3.3 Heat of formation

The enthalpy data of the designed compounds calculated from the vibrational frequency calculation on the optimized geometries obtained at TPSS/6-311G(d,p) are recorded in Table 3. The required energy data needed for the calculation of the heat of formation are given in the Supplementary Information (Table S6). The data recorded in Table 3 show that the heats of formation of all the designed metal complexes are positive and Ni-complexes possess high positive heats of formation as compared to the corresponding Cu-complexes. The results further show that the presence of two nitramide ligands increases the heat of formation. This is in accord with the observation that the presence of explosophores increases the positive heat of formation making the compound more energetic. The increase in the heat of formation in the case of dinitramide complexes may also be due to the fact that the presence of two nitramide groups adjacent to each other would increase the repulsive interaction in comparison to the case when one of the ligand was NH₃. In the case of Ni-complex it is increased by 14.0 kcal/mol as compared to 3.0 kcal/mol in the case of Cu-complex. This may be assigned to the fact that all the Ni–N bonds in the case of Ni(BTA)(NH₂NO₂)₂ are little bit longer than the corresponding Cu–N bonds as recorded in Figure 4. This would ultimately make the Ni-complexes weaker and thus getting an increased positive heat of formation. The heats of formation of the title complexes are found to be in the range of 121–135 kcal/mol. Such a high positive heat of formation associated with the designed molecules yield high performance parameters measured in terms of D and P. However, the specific heat of combustion would be a better estimate of the brisance of the explosive material. The calculated values of the specific heats of combustion of the designed compounds

are also recorded in Table 3. The results show that compounds A1 and B1 are promising and possess values close to 2.0 kcal/g which is comparable to a value of 2.3 kcal/g calculated for RDX and HMX - the two most commonly used explosives.

3.4 Detonation properties

The two most pertinent parameters which are used for assessing the performance and brisance of the high energy materials are the detonation velocity (D) and the detonation pressure (P). These values were calculated using Kamlet–Jacobs equations (4) and (5) and the results are recorded in Table 3. These equations show that detonation parameters are strongly dependent on heat of detonation, Q and the loading density, ρ . The maximum exothermic principle based on the H₂O–CO₂–N₂–metal oxide equilibrium detonation products is indeed an idealistic approach and would overestimate the value of Q. However, Wang *et al.*,²⁴ compared calculated values with K–J equations with the values calculated from recently developed codes like CHEETAH and EXPLOS and concluded that the empirical K–J equations were fairly accurate and there was generally less than 3% difference between the calculated and the experimental values. In order to see the reliability of this method a calculation was performed by Singh *et al.*,⁵ on two reference compounds, RDX and HMX which had widely been used and their experimental values were well known. They concluded that the K–J equations were able to predict values appropriately close to the experimental values. The same procedure is utilized to calculate the values of D and P during the present investigation. These results reveal that D and P values of the designed compounds are in the range of 7.7–8.5 km.s⁻¹ and 29–36 GPa, respectively. The calculated values of the loading density (ρ) for the designed complexes are also recorded in Table 3 and these are found to be in the range of 2.18–2.25 g cm⁻³. These values are significantly higher than the corresponding values for commercial explosives RDX (1.82) and HMX (1.90). Oxygen balance, OB₁₀₀ as listed in Table 3 show that all the

Table 3. Thermodynamic and detonation properties of the title compounds.

Compound	Ω (%)	P (g/cm ³)	Q (cal/g)	D (km/s)	P (GPa)	$\Delta_f H^0$ (kcal/mol)	h ₅₀ (cm)	$\Delta H_{\text{comb,sp}}$ (kcal/g)
A1	–38.22	2.23	776.6	7.76	30.08	104.5	42	1.83
A2	–26.03	2.25	922.1	8.48	36.12	107.5	42	1.49
B1	–38.88	2.18	873.6	7.73	29.47	120.7	42	1.99
B2	–26.42	2.10	1088.0	8.36	33.80	134.7	28	1.66
RDX	–	1.77 1.80*	–	–	–	–	28 (24–28)*	2.30**
HMX	–	1.90 1.90*	–	–	–	–	39 (26–32)*	2.30**

*Experimental values are taken from Ref. 4; **Calculated in the present study.

designed metal complexes are found to have negative oxygen balance and may be mixed with high oxygen content materials such as NH_4NO_3 to increase their brisance. The results show that increasing the number of nitramide ligand drastically increases the oxygen balance. In the case of the dinitramide derivative OB_{100} value is found to be -26.03 for Cu and -26.42 for the Ni-complexes whereas the corresponding values for the mononitramide derivative are -38.88 and -38.22 , respectively. This shows that the dinitramide derivative could be considered to be a preferred compound in terms of the maximum exothermic heat release.

3.5 Impact sensitivity

Based on the electrostatic potential parameters for a variety of high energetic compounds Pospíšil *et al.*,³⁶ devised an empirical relation as given by equation 11 to calculate the values of $h_{50,\text{cm}}$. The electrostatic potential data needed for the calculation of $h_{50,\text{cm}}$ of the designed compounds are given in the Supplementary Information (Table S1). The values of $h_{50,\text{cm}}$ calculated using equation 11 are listed in Table 3. Lower values of $h_{50,\text{cm}}$ signify the compounds to be more sensitive towards impact. In order to assess the reliability of the calculation of impact sensitivity on the basis of equation 11, the same is calculated for known commercial explosives RDX and HMX and these were found to be 28 and 39 cm, respectively. The experimental values of RDX and HMX are reported to be (24,26,28 cm) and (26,29,32 cm), respectively.⁴² The data show that utilizing the methods employed herein, the calculated value of RDX is in close agreement whereas the same for HMX is higher by about 20% (39 with respect to 32). The impact sensitivity is in fact an overall average value that reflects the 50% probability of detonation. However, the data can be used for a relative ease of detonation. Results recorded in Table 3 further show that the value of $h_{50,\text{cm}}$ of the title molecules are in the range of 28–42 cm. The results further show that $\text{Ni}(\text{BTA})(\text{NH}_2\text{NO}_2)_2$ complex having an impact sensitivity of 28 cm would be the most sensitive amongst all the designed metal complexes while other salts are quite insensitive to impact.

4. Conclusions

Theoretical studies have been performed to determine the electronic structure, enthalpy of formation, and detonation characteristics of the BTA-metal complexes of Ni and Cu. The results show that all the complexes yield density in the range of $2.18\text{--}2.25\text{ g cm}^{-3}$. Such

high density compounds accompanied with positive heats of formation $> 100\text{ kcal/mol}$ would be preferred HEDMs. BTA complexes of Ni and Cu have been synthesized by many workers and were found to be stable. The present study reveals that BTA complexes of these metals with nitramide ligand show thermal and kinetic stability at room temperature and Cu-complexes are relatively more stable than those of Ni.

Supplementary Information (SI)

All the detailed information regarding the calculation of heat of formation using atomization method (S1), estimation of heat of detonation (S2), electrostatic parameters for the evaluation of impact sensitivity and crystal density (Table S1), atomic coordinates for the minimized structures (Tables S2–S5), electronic energy of the molecules (Table S6), and optimized structures of the designed complexes, **A1**, **A2**, **B1** and **B2** (Figure S1) are given in the Supplementary Information, available at www.ias.ac.in/chemsci.

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