



A screened hybrid density functional study on energetic complexes: Cobalt, nickel and copper carbohydrazide perchlorates

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ABSTRACT

The molecular geometry, electronic structure, infrared spectra and thermochemical properties of cobalt and nickel tris(carbohydrazide) perchlorates (CoCP and NiCP) as well as copper bis(carbohydrazide) perchlorate (CuCP) were investigated using the Heyd–Scuseria–Ernzerhof (HSE) screened hybrid density functional. The results show that both perchlorate ions coordinate with the copper atom, and the interactions between copper and perchlorate are ionic, whereas all the metal–carbohydrazide interactions are covalent. Due to the delocalization from the σ_{N-H} bond orbital to the n_M^* antibond orbital, the amino stretching vibrations of these complexes show considerable red-shift compared with those of free carbohydrazide ligand. The calculated heats of reaction and formation indicate that the formations of these complexes are exothermic, and the order of their thermal stability is NiCP > CoCP > CuCP. These agree well with the experimental results. Finally, we find that there is a relationship between the energy gap and impact sensitivity.

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1. Introduction

Transition metal perchlorate complexes with nitrogen-rich ligands have attracted considerable attention, since they have superior explosive performances and can be widely used as lead-free primary explosives [1–20]. Carbohydrazide (CHZ) is an interesting azotic ligand with several lone-pair electrons. The structures and properties of its energetic complexes have been extensively studied experimentally [11–20]. There are two different cases for coordination of the CHZ ligand in transition metal CHZ perchlorates. Sinditskii et al. [12] and Zhang et al. [13,15,17,19] investigated their molecular and crystal structures by means of X-ray single crystal diffraction, and reported that CHZ coordinates through the carbonyl O and amino N atoms, forming a five-membered ring. Furthermore, these complexes have six-coordinated octahedron features. Recently, Talawar et al. [20] also characterized the molecular structures of CoCP, NiCP and CuCP by the metal content analysis, IR spectra and electron spectroscopy. As displayed in Fig. 1, CHZ coordinates through both end amino N atoms, forming a six-membered ring. For CoCP and NiCP, three CHZ molecules simultaneously coordinate with the metal atom. However, for CuCP, only two CHZ molecules are coordinated to the copper atom.

From these previously reported experimental results [11–20], we find that, the stretching vibrations of the coordinated amino groups of the CHZ complexes are shifted to lower wave number compared with those of free CHZ ligand. Moreover, perchlorate complexes containing different metal atoms have obvious differences in properties such as thermal stability and impact sensitivity. It is well known that the macroscopic behavior is ultimately controlled by microscopic properties such as the electronic structure and interatomic forces. Thus, there is significant interest in the basic properties of such energetic systems. Additionally, the investigation of the microscopic properties of energetic transition metal complexes remains a challenging task. Theoretical calculations can play an important role in investigating the physical and chemical properties of complex compounds at the atomic level and in establishing the relationships between their structures and properties. To the best of our knowledge, no theoretical work has appeared on the title complexes.

Electronic structure calculations using the HSE screened hybrid density functional produce results which compare very well to experiment for equilibrium structures and properties of both molecules and solids [21–28]. Therefore, in the present work, the molecular geometry, infrared spectra, electronic structure and thermochemical properties of Co, Ni and Cu CHZ perchlorate complexes with the coordination model of six-membered ring are systematically investigated using the HSE functional. Our main purpose here is to examine the differences in the microscopic properties, and to understand their structure–property relationships.

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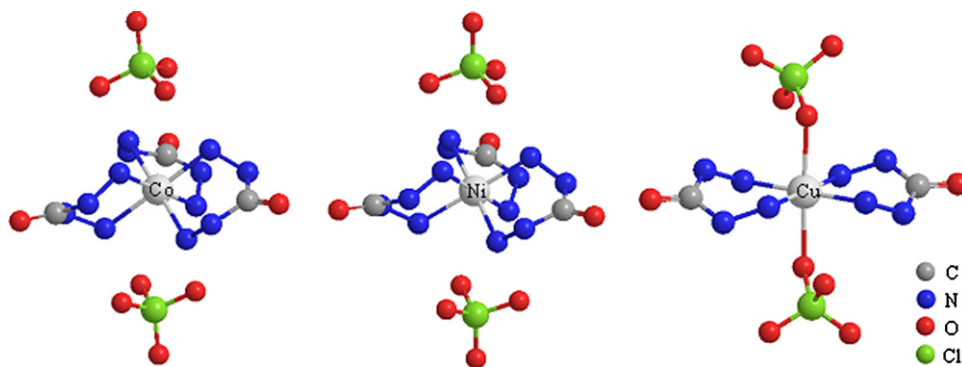


Fig. 1. The optimized structures of CoCP, NiCP and CuCP (hydrogen atoms are omitted for clarity).

2. Computational method

The equilibrium geometries and harmonic vibrational frequencies of CoCP, NiCP and CuCP were calculated using the spin-unrestricted HSE functional [21,22]. The SDD pseudo-potential and basis set [29], that is, the energy-adjusted Stuttgart–Dresden effective core potential together with the [6s5p3d1f] valence basis, was employed on the metal atoms, and the 6-31G** basis set [30,31] was used for the remaining atoms. Some previous theoretical studies [32–34] show that the density functional/SDD basis set combination can reproduce the geometries of transition metal complexes with reasonable accuracy. Natural bond orbital (NBO) analyses [35] were performed subsequently at the same level of theory on each optimized structure. To better understand the metal–ligand bonding scheme, the molecular orbital analyses were also performed on the optimized structures of $[\text{Co}(\text{CHZ})_3]^{2+}$, $[\text{Ni}(\text{CHZ})_3]^{2+}$ and $[\text{Cu}(\text{CHZ})_2]^{2+}$ cations, respectively. Their molecular orbital diagrams were made using the GaussView program.

There are several methods to predict gas phase heats of formation from quantum mechanical calculations [36–42]. One method mainly uses known heats of formation of isolated atoms and calculated atomization energies to predict gas phase heats of formation of molecules [36,37]. Another method is based on Hess' Law [38] and uses a combination of quantum mechanical and experimental information. The third method of predicting gas phase heats of formation is atom and group-equivalent schemes [39–42]. In this work, the gas phase heats of formation of the studied compounds were calculated using the first approach specified in "Thermochemistry in Gaussian" white paper available at <http://www.gaussian.com/g.whitepap/thermo.htm> [37]. Herein, the calculation of heats of formation can be split into a couple of steps. The first step is to calculate the heats of formation of the molecule at 0 K, and it can be expressed as:

$$\Delta_f H^\circ(M, 0\text{ K}) = \sum_{\text{atoms}} x \Delta_f H^\circ(X, 0\text{ K}) - \sum D_0(M) \quad (1)$$

where M stands for the molecule, X represents each element which makes up M , and x is the number of atoms of X in M . $\Delta_f H^\circ(X, 0\text{ K})$ is the heat of formation of the atomic elements at 0 K, and their values are taken from JANAF Thermochemical Tables [43]. $\sum D_0(M)$ is atomization energy of the molecule, which is readily calculated from the total energies of the molecule ($\varepsilon_0(M)$), the zero point energy of the molecule ($\varepsilon_{\text{ZPE}}(M)$) and the constituent atoms:

$$\sum D_0(M) = \sum_{\text{atoms}} x \varepsilon_0(X) - \varepsilon_0(M) - \varepsilon_{\text{ZPE}}(M) \quad (2)$$

The second step is to calculate the heats of formation of the molecule at 298 K:

$$\Delta_f H^\circ(M, 298\text{ K}) = \Delta_f H^\circ(M, 0\text{ K}) + (H_M^\circ(298\text{ K}) - H_M^\circ(0\text{ K})) - \sum_{\text{atoms}} x (H_X^\circ(298\text{ K}) - H_X^\circ(0\text{ K})) \quad (3)$$

where $H_M^\circ(298\text{ K}) - H_M^\circ(0\text{ K})$ and $H_X^\circ(298\text{ K}) - H_X^\circ(0\text{ K})$ are the enthalpy corrections of the molecule and atomic elements, respectively. Because $H_X^\circ(298\text{ K}) - H_X^\circ(0\text{ K})$ does not depend on the accuracy of the heat of formation of the atom, it is the same for both the calculated and experimental data. Here, the enthalpy corrections of atomic elements are obtained from JANAF Thermochemical Tables [43]. The enthalpy correction for the molecule equals $H_{\text{corr}} - \varepsilon_{\text{ZPE}}(M)$, where H_{corr} is the value printed out in the line labeled "Thermal correction to Enthalpy" in Gaussian output.

According to Ref. [37], the number of atoms of each element is the same on both sides of the reaction, all the atomic information cancels out, and so the heats of reaction can be calculated simply by the following equation, which only needs the molecular data:

$$\Delta_r H^\circ(298\text{ K}) = \sum (\varepsilon_0 + H_{\text{corr}})_{\text{products}} - \sum (\varepsilon_0 + H_{\text{corr}})_{\text{reactants}} \quad (4)$$

All of the calculations were carried out with a development version of the Gaussian suite of codes [44].

3. Results and discussion

3.1. Geometric structure

The optimized geometries of CoCP, NiCP and CuCP are shown in Fig. 1. All of them have C_1 symmetry and are energetic minima, that is, they have no imaginary vibrational frequency. As shown in Fig. 1, the optimized structures of CoCP and NiCP are very similar. Three CHZ molecules simultaneously coordinate with the metal atom to form a slightly distorted octahedron. However, CuCP is quite different from them in geometric structure, particularly in the coordination of the perchlorate ions. As previously experimentally reported for $[\text{Cu}(\text{ethylenediamine})_2(\text{nitroformate})_2]$ [45] and $[\text{Cu}(\text{ethylenediamine})_2(5\text{-nitrotetrazolate})_2]$ [46], although only two neutral bidentate ligand molecules are coordinated to the copper atom, the complex also has hexa-coordinated octahedron feature, because both outer anions are also coordinated with the central metal atom.

The selected calculated bond lengths and bond angles of the three complexes are summarized in Table 1. As the bond length of M–N decreases, the bond angle of N–M–N increases. This trend is identical to the CHZ complexes which form five-membered rings

Table 1
The selected bond lengths (Å) and bond angles (°) for the title complexes.^a

Species	M–N	M–O	N–M–N
CoCP	2.160		86.8
NiCP	2.114		88.1
CuCP	2.058	2.295	88.7

^a Values are averaged.

[47,48]. It is noted that the bond length of Cu–O is longer than that of Cu–N though the atomic radius of oxygen is shorter than that of nitrogen [49]. This indicates that the interaction between the Cu and N atoms is much stronger than that between the Cu and O atoms.

3.2. Electronic structure

Natural population analysis was evaluated in terms of natural atomic orbital occupancies. Table 2 shows the atomic charge distribution, electron configuration of the metal atom, as well as the electron occupancy (e_{occ}) and Wiberg bond index (WBI) of M–N bond. Here we can see that the effective valences of the metal atoms approach 1, much smaller than 2, so the metal–ligand interactions in these complexes have strong covalent character. The atomic charge on each coordinated nitrogen atom is about -0.73 , more negative than that of the corresponding nitrogen atom of the free CHZ ligand, indicating charge transfers when CHZ molecule coordinates with the metal atom. Moreover, as previously expected, negative charge of nearly -1 resides on each perchlorate ion.

The formal electron configurations of Co, Ni and Cu atoms are $3d^7 4s^2$, $3d^8 4s^2$ and $3d^{10} 4s^1$, respectively. As shown in Table 2, compared with these formal electron configurations, the 4s populations decrease, whereas almost all of the 3d and 4p populations increase, except the 3d population of Cu atom. This is because the 4s valence orbital of the Cu atom is only occupied by one electron, and it must transfer a few 3d electrons to form the current valence. From detailed NBO analysis, we can conclude that the population excess over the formal configuration mainly arises from strong donations from lone-pair electrons on the coordinated nitrogen atoms, as well as $\sigma_{\text{N-H}}$ and $\sigma_{\text{N-N}}$ bond orbitals of the ligands.

The WBI arises from the manipulation of the density matrix in the orthogonal natural atomic orbital basis derived through the natural population analysis. The WBI expresses the sum of squares of density matrix elements and relates to the bond characteristic closely [50,51]. As presented in Table 2, the WBIs of M–N bonds are larger than 0.28, and the e_{occ} of M–N bonding orbitals are close to 1. Thus, the bonding between the metal atoms and the CHZ ligands is covalent. However, the average WBI of Cu–O is only 0.19, much smaller than that of Cu–N. Additionally, there is no Cu–O bonding orbital. Therefore, the interaction between the Cu atom and the perchlorate ion is ionic in nature and the electrostatic interaction dominates the corresponding metal–ligand interaction [47,48].

Table 2

Atomic charge on each metal atom, coordinated N atom and perchlorate ion; electron configuration of the metal atom; as well as e_{occ} and WBI of M–N bond for the studied compounds.^a

Species	Atomic charge			Electron configuration			M–N	
	M	N	ClO ₄	4s	3d	4p	e_{occ}	WBI
CoCP	0.840	−0.741	−0.862	0.29	7.28	0.50	0.983	0.281
NiCP	0.764	−0.729	−0.861	0.29	8.33	0.53	0.984	0.291
CuCP	0.858	−0.726	−0.793	0.33	9.29	0.47	0.973	0.300

^a Values are averaged except the natural population of the metal atom.

To further study the characteristic of M–N bonds, a detailed NBO analysis of $[\text{Co}(\text{CHZ})_3]^{2+}$, $[\text{Ni}(\text{CHZ})_3]^{2+}$ and $[\text{Cu}(\text{CHZ})_2]^{2+}$ is performed. Their molecular orbital pictures made using the GaussView program are displayed in Fig. 2. Apparently, their highest occupied molecular orbitals (HOMOs) mainly represent nonbonding orbitals occupied by the lone-pair electrons of the O and N atoms, and the nonbonding 3d orbitals of the metal atoms. HOMO_{−10} for $[\text{Co}(\text{CHZ})_3]^{2+}$ and $[\text{Ni}(\text{CHZ})_3]^{2+}$ and HOMO_{−12} for $[\text{Cu}(\text{CHZ})_2]^{2+}$ are π -bond orbitals largely responsible for the coordinate bonding between the central atom and the vicinal N atoms. For $[\text{Co}(\text{CHZ})_3]^{2+}$ and $[\text{Ni}(\text{CHZ})_3]^{2+}$, the covalent π bonds arise from a valence bonding electron density overlap between the sp^3d^2 hybridization valence orbitals of the metal atom and the $sp^{2.5}$ hybridization coordinated N atoms. For $[\text{Cu}(\text{CHZ})_2]^{2+}$, the π bonds result from the same interactions, but the Cu and adjacent N atoms have sp^2d and $sp^{3.5}$ hybridizations, respectively. Note that, for all of the three complex cations, the valence bonding electron is predominantly donated by the coordinated N atoms, with only about 10% localization on the central metal atom.

3.3. Infrared spectra

To investigate the influence of coordination on vibrational properties, we compared the simulated infrared spectra of the three complexes with that of free CHZ ligand (see Fig. 3). Since density functional methods usually overestimate the harmonic vibrational frequencies and no scale factor is available for the HSE level of theory, all theoretical frequencies reported here are listed as calculated and are slightly larger than the experimental data [20]. From Fig. 3, it can be found that the IR spectra of CoCP and NiCP are almost the same, but that of CuCP is somewhat different from them. This is because CuCP differs obviously from CoCP and NiCP in geometric structure. Herein, only some typical vibrational modes were analyzed and discussed. For individual CHZ ligand, the strong absorption peak observed at 1837 cm^{-1} is raised from the stretching vibrations of carbonyl group. The two weak peaks about 3504 and 3674 cm^{-1} can be assigned to the symmetric and asymmetric stretching vibrations of the amino group, respectively. For the three complexes, the IR stretching band corresponding to the carbonyl group almost remains unchanged, in line with the structural feature that the carbonyl oxygen atoms do not coordinate with the metal atom. However, as shown in Fig. 3, the symmetric and asymmetric stretching vibrations of NH_2 are shifted to lower wave number (around 3350 and 3560 cm^{-1} , respectively, or 3330 and 3500 cm^{-1} for CuCP) compared to those of free CHZ ligand. This trend of vibrational frequency is in good agreement with the experimental result [20] and it theoretically confirms that FTIR is an effective and reliable method to characterize the coordination model.

Why do the amino stretching vibrations in the complexes show considerable red-shift? This is due to donor–acceptor (bond–antibond) interactions between the ligand and the metal atom, especially the delocalization from $\sigma_{\text{N-H}}$ bond orbital to n^*_M antibond orbital [47,48]. As can be seen from Table 3, the e_{occ} of the localized $\sigma_{\text{N-H}}$ bond orbital decreases as CHZ coordinates with the metal atom. Subsequently, the resulting bond length increases, but the WBI and vibrational frequency decrease remarkably.

Table 3

Bond length (b , Å), e_{occ} and WBI of amino N–H bond of the free CHZ ligand and its complexes.^a

Species	e_{occ}	b	WBI
CHZ	1.992	1.018	0.824
CoCP	1.983	1.024	0.746
NiCP	1.983	1.025	0.745
CuCP	1.983	1.027	0.744

^a Values are averaged.

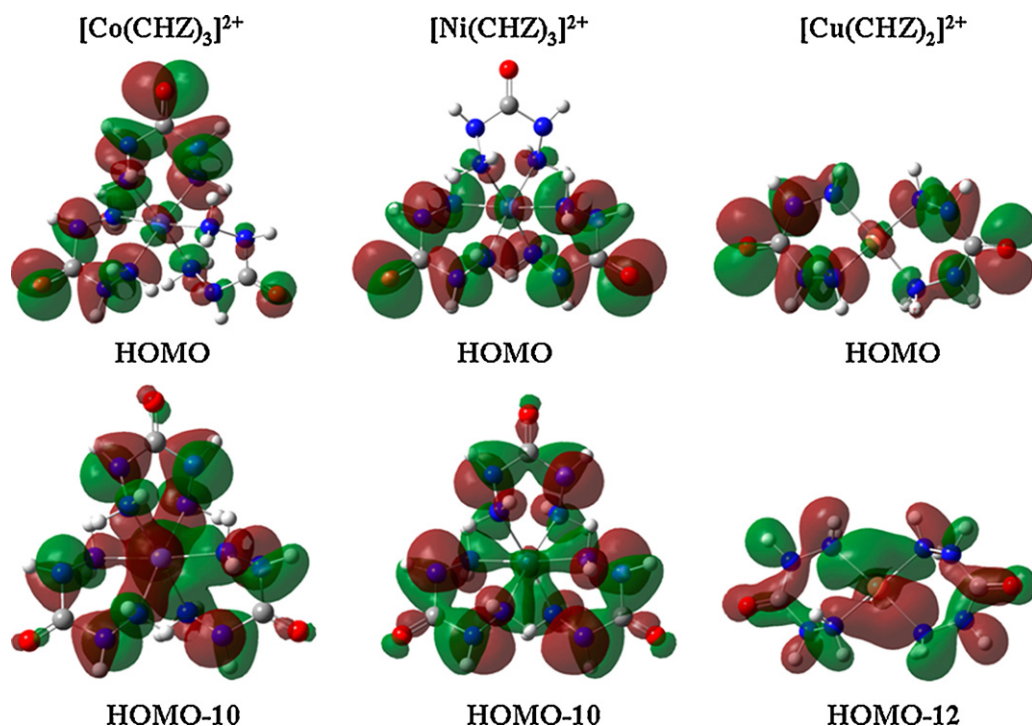


Fig. 2. Some molecular orbital pictures of $[\text{Co}(\text{CHZ})_3]^{2+}$, $[\text{Ni}(\text{CHZ})_3]^{2+}$ and $[\text{Cu}(\text{CHZ})_2]^{2+}$.

3.4. Heats of reaction and formation

The metal CHZ perchlorates are experimentally synthesized by the following reaction: $\text{M}(\text{ClO}_4)_2 + n\text{CHZ} \rightarrow [\text{M}(\text{CHZ})_n](\text{ClO}_4)_2$ [13,15,17,19,20]. For CoCP and NiCP, n equals 3; for CuCP, n equals 2. Here, we calculated the heats of reaction of the aforementioned reactions using Eq. (4). The corresponding computed heats of reaction are listed in Table 4. It can be seen that all the values of the heats of reaction are negative. Therefore, the formations of these complexes are exothermic, which is in agreement with the experimental result [20].

Table 4

Calculated heats of reaction ($\Delta_r H^\circ$, kcal/mol) and formation ($\Delta_f H^\circ$, kcal/mol) at 298 K, and experimental initial decomposition temperature (T_i , °C) of the three complexes.

Species	CuCP	CoCP	NiCP
$\Delta_r H^\circ$	-44.7	-68.9	-88.4
$\Delta_f H^\circ$	103.3	59.6	54.9
T_i	120	220	260

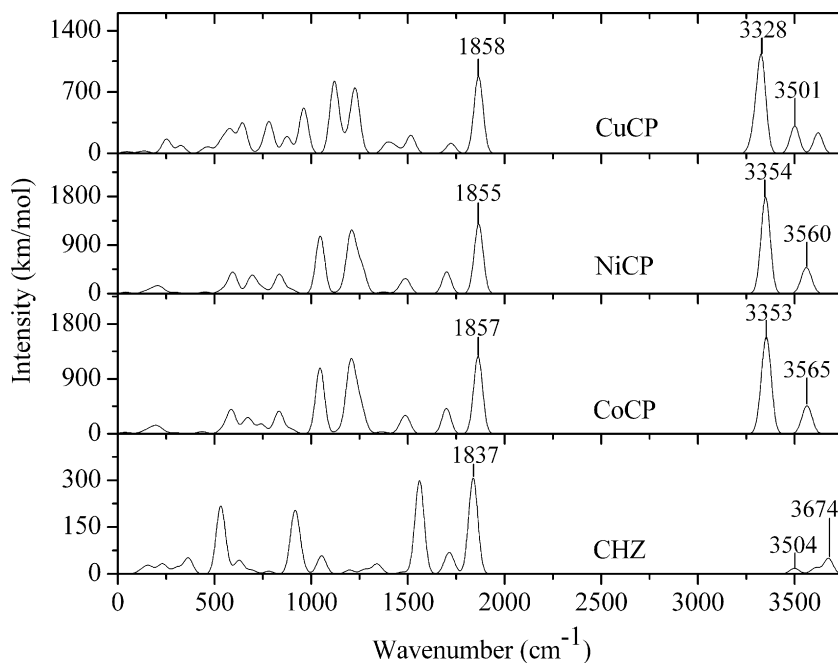


Fig. 3. The calculated IR spectra of free CHZ ligand and its complexes.

It is well known that the evaluation of explosive performances of energetic materials requires the knowledge of the heats of formation. Unfortunately, it may be impractical or dangerous to measure the heats of formation of energetic materials and unstable compounds experimentally. However, the computational approaches have shown great advantages for obtaining the heats of formation of these demanding materials [52–57]. A previous theoretical study [58] in which the heats of formation are also computed using the method specified in “Thermochemistry in Gaussian” white paper reveals that the inclusion of exact exchange terms in DFT methods generally results in more consistently accurate results for the heats of formation of transition metal systems. Therefore, the presented heats of formation calculated at the HSE/SDD/6-31G** level of theory are accurate and reliable. The gas phase heats of formation of the studied compounds are shown in Table 4 together with their experimental initial decomposition temperature [20]. The heats of formation of CoCP, NiCP and CuCP are positive, indicating that these three compounds are thermodynamically unstable in gas phase. Furthermore, heat of formation is one of the important factors that go into thermal stability. Just according to the calculated heats of formation, we can conclude that NiCP is the most stable; CuCP is the least stable; and CoCP has the moderate stability. Obviously, this theoretical thermal stability order agrees well with the experimental thermal stabilities deduced from the initial decomposition temperature [20].

3.5. Correlation of energy gap with impact sensitivity

In this section, an attempt is made to correlate the impact sensitivity of the three complexes with their electronic structure. The energy gap between the HOMO and LUMO (lowest unoccupied molecular orbital) is an important parameter to characterize the electronic structure of molecules. Gilman [59–62] has emphasized the role of energy gap closure in the explosion of molecules suffering shear strain. It is well known that the HOMO–LUMO gap retains close connection to some molecular properties. Here we discuss the correlation of energy gap with impact sensitivity. The energy gaps of the three complexes computed using the HSE functional are listed in Table 5 along with their experimental impact sensitivities [20]. Energetic materials with smaller $h_{50\%}$ value are more sensitive to impact. Thus, from Table 5, it can be seen that the HOMO–LUMO gap increases in the order of CuCP, CoCP, NiCP, while the experimental impact sensitivity decreases in the following sequence: CuCP > CoCP > NiCP. That is to say, the smaller energy gap corresponds to the higher impact sensitivity. The initiating reaction of detonation due to external mechanical stimulus is taken to be an electronic excitation process [63–65], thus a possible explanation may be that the smaller the energy gap, the easier the electron transfers from the HOMO to the LUMO and the easier the energetic molecule explosively decomposes.

A previous investigation has also shown [66] that there is a reasonable correlation between the impact sensitivity of 50 organic explosives and the HOMO–LUMO energy gap. In periodic solids, of course, the HOMO and LUMO form the valence band and the conduction band, respectively. So the equivalent of HOMO–LUMO gap is the band gap. Numerous theoretical studies [67–74] on the energetic solids have shown that the band gap can be correlated with the impact sensitivity. Beyond all doubt, these observations and results

strongly support our conclusion here that there is the relationship between the energy gap and impact sensitivity.

4. Conclusions

We have performed a detailed density functional theory study of the geometry, electronic structure, infrared spectra, and thermochemical properties of CoCP, NiCP and CuCP. The obtained results show that all of the three complexes have six-coordinated octahedron features. Both perchlorate ions also coordinate with the copper atom. Detailed NBO analyses indicate that the Cu–O coordination bonds are ionic in nature, whereas the M–N coordination bonds are covalent, and the bonding electron is predominantly donated by nitrogen. As previously reported in experiment, the stretching vibrations of amino group show considerable red-shift because of the donor–acceptor interactions between the ligand and metal atom. The calculated thermochemical properties indicate that the formations of these complexes are exothermic and the order of their thermal stability is NiCP > CoCP > CuCP. These are in agreement with the experimental results. It is also found that there is a relationship between the energy gap and impact sensitivity for the three complexes.

Acknowledgments

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Table 5

Calculated energy gap (ΔE , eV) and experimental impact sensitivity ($h_{50\%}$, cm) for the studied complexes.

Species	CuCP	CoCP	NiCP
ΔE	3.59	4.55	5.80
$h_{50\%}$	11	55	60

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