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ORIGINAL PAPER

Theoretical studies on densities, stability and detonation properties of 2D polymeric complexes $Cu(DAT)_2Cl_2$ and its new analogues $Zn(DAT)_2Cl_2$

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Abstract A novel environmentally friendly octahedrally coordinated 2D polymeric complexes bis(1,5-diaminotetrazole) -dichlorozinc(II) ($Zn(DAT)_2Cl_2$) was first designed based on the the crystal data of bis(1,5-diaminotetrazole)- dichlorocopper(II) ($Cu(DAT)_2Cl_2$). Density functional theory (DFT) was used to predict the optimized geometries at TPSSTPSS/6-311G(d, p) level. Densities and detonation properties were evaluated using the electron cloud enclosed volume and VLW equation of state (VLW EOS), respectively. Calculation results show that the density of $Zn(DAT)_2Cl_2$ ($2.117\ g\cdot cm^{-1}$) is a bit more than that of $Cu(DAT)_2Cl_2$ ($2.106\ g\cdot cm^{-1}$). The calculated high positive heat of formation (HOF) predicts that the stabilities of the title compounds decrease in the order $Zn(DAT)_2Cl_2 > Cu(DAT)_2Cl_2$, which agrees with the result of bond dissociation energies (BDE). Even though they have the same molecule structures, their first scission steps are different. Furthermore, the title two compounds show good detonation velocities and pressures compared with that of bis-(5-nitro-2*H*-tetrazolato-N^2) tetraamminecobalt(III) perchlorates (BNCP), and they are potential candidates for high-energy-density materials (HEDM).

Keywords Coordination polymers · Heats of formation · Sensitivity · Tetrazole energetic metal complexes · VLW

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Introduction

Due to the excellent performance and distinctive structure characteristics, metal tetrazolate complexes application as energetic materials are of current interest [1–3]. The structure and properties such as acceptable stability, sensitivity and suitable explosive performance of the compounds remained elusive by experimental methods, and the inquiry into the solid-state molar enthalpy of formation has not been reported in the literatures [4]. A great variety of tetrazoles especially functionally substituted ones are investigated as ligands, in which 5-substituted tetrazoles are the most readily available tetrazole derivatives [5–9].

Bis-(5-nitro-2*H*-tetrazolato-N^2) tetraamminecobalt(III) perchlorates (BNCP) is an energetic lead-free initiator. It is very safe to handle, thermally stable (264 °C) and it has a high velocity of detonation ($8.1\ km\cdot s^{-1}$) at density of $1.97\ g\cdot cm^{-1}$ (calculated by Smirnov [10]). However, the production cost of BNCP is expensive. 1,5-Diamino-tetrazole (DAT) has a high nitrogen content, positive enthalpy of formation, and good thermal stability [6], and five of the six nitrogen atoms in its molecular structure are able to bind metal ions [7]. Many researchers suggested it to be a promising ligand that can combine with transition metals to form energetic coordination compounds [7–20]. Recently, Zhang [7, 13–16] has synthesized a serial of metal energetic complex with 1,5-diamino-tetrazole (DAT).

In 2005, Gaponik et al. [20] synthesized a new environmentally friendly octahedrally coordinated 2D polymeric complexes bis(1,5-diaminotetrazole)- dichlorocopper (II) ($Cu(DAT)_2Cl_2$, Fig. 1). They reported its crystal structure, magnetic susceptibility and thermal properties. The thermal analysis noted that $Cu(datz)_2Cl_2$ with decomposition temperature 160 °C was less stable than the free ligand DAT [21]. It

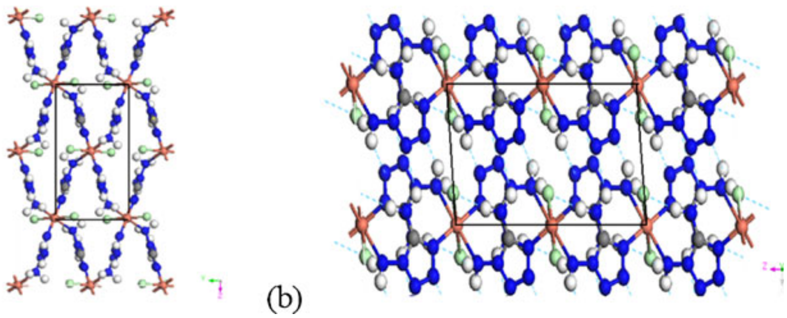

Fig. 1 **a** The crystal structure of Cu(DAT)$_2$Cl$_2$ viewed along the a-axis. **b** The crystal structure of Cu(DAT)$_2$Cl$_2$ viewed along the b-axis

should be pointed out that those are not N–H…N reported by Gaponik et al. but N–H…Cl intermolecular hydrogen bonds between the above networks in Fig. 1b. The intermolecular hydrogen bonds between the networks can increase stability of the crystal. Remaining hydrogen bonds, such as N–H…N, operate within the polymeric layers.

For the nature of insensitive and coordination ability, complexes with zinc ions as the central coordination ions have been studied by more and more scientists [3, 11, 16, 22]. Sensitivity data indicated that the Co/Ni/Cu complexes are more friction sensitive (3–4.8 kg) than mono-(5-nitro-H-tetrazolato-N)triammine zinc(II) perchlorate (14 kg) [11].

In this paper, a novel environmentally friendly primary explosives research is expanded here to bis(1,5-diaminotetrazole)-dichlorozinc (II) (Zn(DAT)$_2$Cl$_2$). To determine the energetic information of Zn(DAT)$_2$Cl$_2$ and Cu(DAT)$_2$Cl$_2$, we focus on the densities, heat of formation, electronic structures, bond dissociation energies and detonation properties of these two compounds by theoretical methods.

Computational methods

The kinetic energy density-dependent generalized gradient approximation (meta-GGA) functional Tao-Perdew-Staroverov-Scuseria (TPSS) [23–26] as implemented in the Gaussian 09 program package [27], was used for the geometry optimization of Cu(DAT)$_2$Cl$_2$ (Fig. 2). All the optimized structures were characterized to be true relative energy minima of the potential surfaces by frequency calculations (no imaginary frequencies were found). The optimized structure data in Table 1 shows that it will be a good choice to study the structure of Zn(DAT)$_2$Cl$_2$ at TPSSTPSS/6-311G(d, p) level.

Based on the optimized geometries, the other properties of the title compound, such as heats of formation, molecular electrostatic potential and thermal decomposition, were calculated and discussed below.

Density calculations

Calculation for the densities of the title metal complexes was performed by the DMol^3 program. The exchange-correlation interaction was treated by functional Perdew, Burke and Ernzerh of generalized gradient approximation (PBE GGA) [24, 28–32], and applied basis set was double numerical basis set plus d-functions (DND). At first, the enclosed volume (V_{en}) of electron cloud around the molecule was calculated based on each optimized structure. Then ρ_{en} was obtained by the following equation [33]:

$$\rho_{en} = \frac{M_W}{V_{en}\cdot 6.02\cdot 10^{23}\cdot \left(10^{-8}\right)^3} = \frac{M_W}{V_{en}\cdot 0.602} \quad \left(g/cm^3\right), \tag{1}$$

where M_w is the molecule weight, g·mol^{-1}. V_{en} stands for the enclosed volume of electron cloud around the molecule, nm. It should be noted that actually there are four DAT molecule and two chlorine ions coordinated with every zinc ion or copper ion, so the value of M_w should contain the four DAT molecule, two chlorine ions and one metal ion.

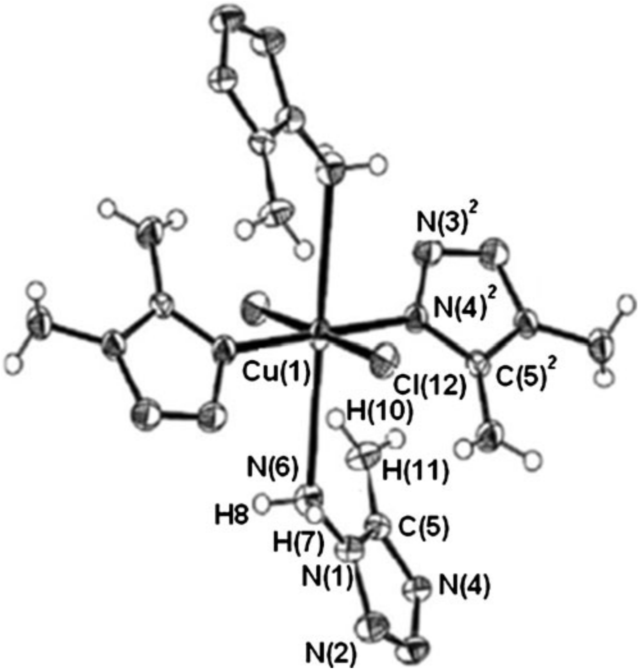

Fig. 2 Coordination environment of the copper ion in Cu(DAT)$_2$Cl$_2$ (Atom labels correspond to the asymmetric unit, ellipsoids are drawn at the 50 % probability level)

Table 1 Selected bond lengths (nm) and angles (°) for Cu(DAT)$_2$Cl$_2$ at UTPSSTPSS/6-311G(d, p) level

Cu(DAT)$_2$Cl$_2$	Comp.	Exp. [15]		Comp.	Exp. [20]
Bond lengths					
N(1)-N(2)	0.138	0.136	Cu(1)-Cl(12)	0.236	0.231
N(1)-C(5)	0.136	0.135	Cu(1)-N(6)	0.259	0.274
N(1)-N(6)	0.140	0.140	Cu(1)-N(4)^2	0.201	0.198
N(2)-N(3)	0.129	0.128			
N(3)-N(4)	0.138	0.137			
N(4)-C(5)	0.135	0.134			
C(5)-N(9)	0.133	0.133			
Bond angles					
N(2)-N(1)-C(5)	109.216	109.31	N(6)-Cu(1)-Cl(12)	90.544	89.27
N(2)-N(1)-N(6)	126.898	124.70	N(6)-Cu(1)- N(4)^2	89.115	96.58
C(5)-N(1)-N(6)	123.103	125.78	Cl(12)-Cu(1)-N(1)	88.863	89.78
N(1)-N(2)-N(3)	106.215	106.76	N(4)^2-Cu(1)-C(5)^2	129.09	131.38
N(2)-N(3)-N(4)	111.296	110.36	N(4)^2-Cu(1)- N(3)^2	121.221	121.46
N(3)-N(4)-C(5)	106.49	107.14			
N(1)-C(5)-N(4)	106.677	106.42			
N(1)-C(5)-N(9)	123.502	125.53			
N(4)-C(5)-N(9)	128.000	127.93			

Heat of formation (HOF)

In this work, the calculation of HOF was based on atomization Scheme 1 [34, 35]. Zhou [36] has efficiently and successfully obtained the HOF of high-nitrogen energetic substituted s-tetrazine compounds.

HOF of M at 298 K was calculated at the DFT/TPSSTPSS/6-311++G(d, p)//TPSSTPSS/6-311G(d, p) level [37].

Finally, the HOF values were calculated using our own computer code.

Bond dissociation energies (BDE)

The bond dissociation energy of the molecule corresponds to the enthalpy of reaction, which is the energy required for homolytic bond cleavage at 298 K and 1 atm [38–41]. Based on the weakest bond principle, as a means of further exploring the first step of decomposition of Zn(DAT)$_2$Cl$_2$ (Fig. 3), the X-Zn bond dissociation energy for the cleavage reaction of RX-ZnR$^{'}$ → RX• + ZnR$^{'}$• was calculated at the UTPSSTPSS/6-311++ G(d, p)//UTPSSTPSS/6-311G(d, p) level as:

$$\mathrm{BDE} = \mathrm{E}(\mathrm{RX}\bullet) + \mathrm{E}\left(\mathrm{ZnR}\dot{\bullet}\right) - \mathrm{E}\left(\mathrm{RX} - \mathrm{ZnR}'\right), \tag{2}$$

where E is the total energy. RX-ZnR$^{'}$ is the Zn(DAT)$_2$Cl$_2$. RX stands for Cl ion or DAT molecule. When RX is DAT molecule, X is DAT(N6) or DAT(N4), and R stands for the rest part of DAT molecule, respectively. The X-Zn bond dissociation energy (BDE$_{\mathrm{ZPE}}$) corrected for zero point energy (ZPE) is:

$$\mathrm{BDE}_{\mathrm{ZPE}} = \mathrm{BDE} + \mathrm{ZPEC}, \tag{3}$$

where ZPEC is the zero point energy correction.

Detonation properties calculations

All detonation properties were calculated by our developed VLW code including the VLW EOS (Scheme 2) [42–44], law of mass conservation, law of momentum conservation, law of energy conservation and C-J detonation conditions [45]. In Scheme 2, N, *k* and *T** is Avogadro constant, Boltzmann constant and the nondimensional temperature, respectively. σ and ε are the Lennard-Jones potential parameters. The VLW code only needs the chemical compositions, heats of formation, and densities of compounds as input, and can calculate the detonation velocities, pressures and heats of the solid, liquid and gaseous explosives and propellants.

Scheme 1 The atomization scheme

$$\begin{tikzcd}
c\mathrm{C} + h\mathrm{H} + n\mathrm{N} + o\mathrm{O} + m\mathrm{MT} + n\mathrm{Cl} \arrow[r, "\Delta H_f^0(\mathrm{M},298\,\mathrm{K})"] \arrow[d, "\sum_{\mathrm{atom}} x(H_X^0(0\,\mathrm{K}) - H_X^0(298\,\mathrm{K}))"] & \mathrm{M} \\
c\mathrm{C}^0 + h\mathrm{H}^0 + n\mathrm{N}^0 + o\mathrm{O}^0 + m\mathrm{MT}^0 + n\mathrm{Cl}^0 \arrow[r, "\Delta H_f^0(\mathrm{M},0\,\mathrm{K})"] & \mathrm{M}^0 \arrow[u, "H_M^0(298\,\mathrm{K}) - H_M^0(0\,\mathrm{K})"']
\end{tikzcd}$$

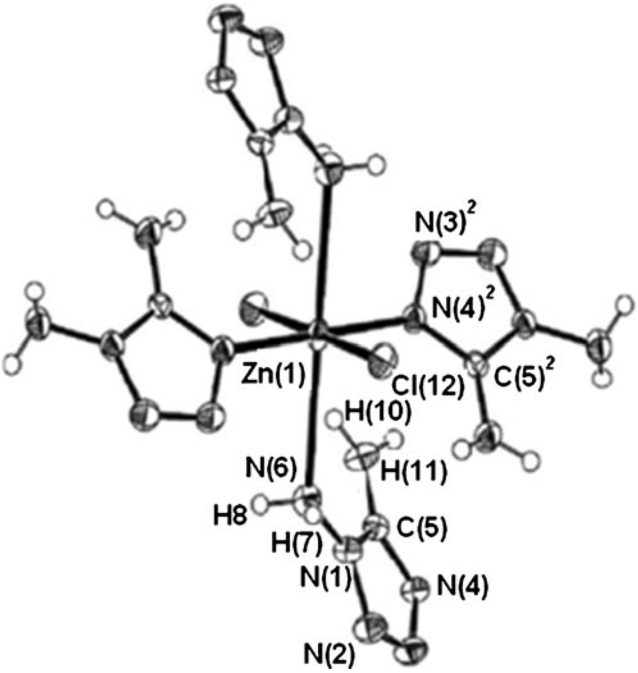

Fig. 3 Coordination environment of the zinc ion in Zn(DAT)$_2$Cl$_2$ (Atom labels correspond to the asymmetric unit, ellipsoids are drawn at the 50 % probability level)

Results and discussion

Molecular geometries

Selected bond lengths and angles for Zn(DAT)$_2$Cl$_2$ (Fig. 3) compared with those in optimized molecule of DAT are given in Table 2. It should be pointed out that coordination environment of the copper ion in Zn(DAT)$_2$Cl$_2$ is similar to that of Cu(DAT)$_2$Cl$_2$ (Fig. 3). DAT acts as bridging ligand coordinated by two different metal zinc ion through the N(4) atom of the DAT tetrazole ring and the N(6)nitrogen atom of the 1-amino group. N(6) atom is not conjugated with the π-system of the tetraze ring, but available for metal binding.

Table 2 Display partial bond lengths of the optimized geometry for the titled compounds from DFT-TPSSTPSS calculations

Bonds	DAT	Zn(DAT)$_2$Cl$_2$	Cu(DAT)$_2$Cl$_2$
N(1)-N(2)	0.137	0.138	0.138
N(1)-C(5)	0.135	0.136	0.136
N(1)-N(6)	0.139	0.142	0.141
N(1)^2-N(6)^2	0.139	0.139	0.139
N(3)^2-N(4)^2	0.137	0.139	0.139
N(4)^2-C(5)^2	0.132	0.135	0.135
Cl(12)-MT		0.245	0.236
N(4)^2-MT		0.218	0.201
N(6)- MT		0.224	0.259

MT stands for copper ion or zinc ion

There is some elongation in the complex molecule of N(1)–N(6), N(3)^2-N(4)^2 and N(4)^2-C(5)^2 bonds by 0.003 nm, 0.003 nm and 0.002 nm, respectively. The elongations may be caused by the coordination effect. As an electron donor, the zinc ion makes the electron density around N(4) and N(6) increase. Accordingly, the negative charges of N(4) and N(6) increase, and then the length of those three bonds becomes longer because of electrostatic repulsion. Surprisingly, in molecule Zn(DAT)$_2$Cl$_2$ the bong lengths increase in the order N(4)^2-Zn(47) (0.218 nm) < N(6)-Zn(47) (0.228 nm) < Cl(12)-Zn(47) (0.245 nm), which is different from that of N(4)^2- Cu(1) (0.201 nm) < Cl(14)-Cu(1) (0.236 nm) < N(7)- Cu(1) (0.259 nm) in molecule Cu(DAT)$_2$Cl$_2$. In Table 2, the bond length of N(6)-Zn(1) (0.224 nm) is much shorter than that of N(6)-Cu(1) (0.259 nm), so molecule Zn(DAT)$_2$Cl$_2$ might be more stable than molecule Cu(DAT)$_2$Cl$_2$.

Electronic structure and electrostatic potential

NBO analysis was carried out to study the electronic structure and molecular stability by calculating the Wiberg bond order (Table 3), which can be used to evaluate the strength of a covalent bond and further the stability of a covalent compound, at TPSSTPSS/6-311++G(d, p) level based on the optimized geometry.

The data in Table 3 show that participation of the tetrazole ring and N(6) nitrogen atom of the 1-amino group in coordination renders only an inappreciable influence on stability of DAT molecule.

The Wiberg bond order of the atoms coordinating with metal atoms zinc ion(0.413, 0.228 and 0.173) and cooper ion (0.442, 0.284 and 0.117) are even less than that of the N-H bond in DAT. N(1)-N(6) bond is the weakest bond in molecule D which can explain why Cu(DAT)$_2$Cl$_2$ or Zn(DAT)$_2$Cl$_2$ is less stable than the free ligand DAT.

The natural electron configuration (NEC) values of the metal ion Zn and Cu in Table 4 indicate that the donor-acceptor interactions between the ligands and metal cations

Scheme 2 The VLW equation of state

$$\frac{pV}{\mathrm{R}T} = 1 + B^*(T^*)w + \frac{B^*(T^*)}{T^{*1/4}} \sum_{n=3}^{m} \frac{w^{(n-1)}}{(n-2)^n}$$

$$B^*(T^*) = \sum_{j=0}^{\infty} b^{(j)} T^{*-(2j+1)/4} \; ; \; b^{(j)} = -\frac{2^{j+1/2}}{4j!} \prod \left(\frac{2j-1}{4} \right); \; b_0 = \frac{2}{3}\pi N\sigma^3; \; T^* = \frac{kT}{\varepsilon}; \; w = \frac{b_0}{V}$$

Table 3 Wiberg bond order of partial DAT, $Zn(DAT)_2Cl_2$ and $Cu(DAT)_2Cl_2$ bonds

	N(1)-N(6)	N(6)-H(7)	N(6)-H(8)	N(9)-H(11)	$N(3)^2$-$N(4)^2$	$N(4)^2$-$C(5)^2$	$C(5)^2$-$N(9)^2$
DAT	1.033	0.842	0.842	0.822	1.280	1.454	1.172
$Zn(DAT)_2Cl_2$	1.002	0.796	0.812	0.743	1.223	1.314	1.300
$Cu(DAT)_2Cl_2$	1.014	0.818	0.831	0.752	1.222	1.303	1.287
	$N(9)^2$-$H(10)^2$	MT-Cl(12)	MT-N(6)	MT-$N(4)^2$	NEC of copper ion or zinc ion		
DAT	0.824	0.413	0.173	0.228	4 s	3d	4p
$Zn(DAT)_2Cl_2$	0.738	0.442	0.117	0.284	0.45	9.98	0.59
$Cu(DAT)_2Cl_2$	0.742				0.37	9.43	0.52

MT stands for copper ion or zinc ion. NEC is the natural electron configuration

for $Zn(DAT)_2Cl_2$ (or $Cu(DAT)_2Cl_2$) the number of electrons on 4s, 3d, 4p orbital is 0.45, 9.98 and 0.59 (or 0.37, 9.43 and 0.52), respectively. The formation of +0.646 eV copper ion and +0.946 eV zinc ion results in the decreasing of number of electrons on 4s and 3d orbitals of molecules $Cu(DAT)_2Cl_2$ and $Zn(DAT)_2Cl_2$.

The Wiberg bond order values in Table 5 also tell us that Zn-Cl bond is predominantly ionic in nature, but it also contains strong covalent property with the Wiberg bond order 0.41. What's more, the interaction between Zn-Cl is stronger than Zn-N(6) and Zn-$N(4)^2$, in respect that the Wiberg bond order of Zn-Cl bond is larger.

By MO calculations of molecular electrostatic potential (MESP) and energies of hydronation of nitrogen atoms in DAT, Gaponik [21] has investigated the possible coordination sites in the DAT molecule under formation of complex compounds. In this work, NBO charge analysis will be more simple and reasonable to study the possible coordination sites. Figure 4 shows that the NBO charge on N4, N6 and N7 with the three most negative values is −0.378, −0.627 and −0.791, respectively. It is obvious that N7 atom is conjugated with the π-system of DAT tetrazole ring, and it is impossible for N7 to coordinate with other atoms. Finally, N4 and N6 atoms are the possible coordination sites, and this result can be testified by the reported crystals structures of complexes [7, 11–13].

In some cases, $V_{\mathrm{MEP}}(r)$, which is the net electrostatic effect resultant from the total molecular charge distribution (nuclei plus electrons), allows to predict successfully the coordination sites in molecules under formation of complex compounds at any point r by the nuclei and electrons of a molecule [46].

$$V_{\mathrm{MEP}}(r) = \sum_{k}^{\text{nuclei}} \frac{Z_k}{|r - r_k|} - \int \psi(r') \frac{1}{|r - r'|} dr', \qquad (4)$$

where Z_k is the charge on nucleus k located at r_k. The sign of $Z_k/|r-r_k|$ indicates thus the electrostatic potential of nucleus k located at r_k. $\int \psi(r') \frac{1}{|r-r'|} dr'$ stands for the negative electrostatic potential at r_k where all the negative charge dominates.

The molecular electrostatic potential surface for the title tetrazole energetic metal complexes (TEMCs) molecules calculated at TPSSTPSS/6-311++G(d,p) level of theory are given in Fig. 5.

The molecular electrostatic potential images (Fig. 5) show that most of the positive electrostatic domains appear over the DAT molecules, and the negative spatial domains of the two TEMCs over the periphery of DAT ring and two Cl ions. In the center both the positive and negative MESP spatial domains are much weaker than that of other domains, which demonstrates that the initial decomposition locations should be bonds connecting with the central metal ions directly. This conclusion agrees with that of molecular geometry above. The two Cl ions have the most negative electrostatic potentials. It should be noted that the largest negative value of MESP surface does not necessarily correspond to the atom with the

Table 4 Bond dissociation energies and bong lengths of title compounds computed at TPSSTPSS/6-311G(d, p) level

	E(298 K)/(Hartree)	ZPEC/(Hartree)	$BDE_{ZPE}/(kJ\cdot mol^{-1})$	Bond lengths/(nm)
Cu-Cl	−3577.340	0.323	178.532	0.236
Cu-N(6)	−3668.452	0.244	199.536	0.259
Cu-$N(4)^2$	−3668.442	0.245	225.7904	0.201
Zn-Cl	−3716.075	0.321	472.585	0.245
Zn-N(6)	−3807.303	0.244	191.659	0.224
Zn-$N(4)^2$	−3807.295	0.244	212.663	0.218

Table 5 Lennard-Jones potential parameters of Co, Cu and Zn metals

Metals	σ/(A)	$\varepsilon/(k\cdot K^{-1})$	$b_0/(ml\cdot mol^{-1})$
Co[50]	2.506	8591.286	19.855
Cu[51]	2.549	4125.700	20.877
Zn[52]	2.000	2204.800	10.088

In the detonation products Co and Cu are liquids, and Zn is gas

largest negative charge. In many energetic systems the regions of positive potential are always larger in area and stronger than that of the negative, in contrast to the situation in usual non-energetic organic compounds. Obviously, these two TEMCs may possess property of high energy.

Molecular stability

The stability of a high energetic insensitive explosive was emphasized [47]. The bond dissociation energies (BDE_{ZPE}) of $Cu(DAT)_2Cl_2$ and $Zn(DAT)_2Cl_2$ are listed in Table 4.

It is obvious that the length of bond Zn-Cl is longer than that of bond Cu-Cl, but the BDE_{ZPE} of the former is more than that of the latter. The scission of $Cu(DAT)_2Cl_2$ may start from the scission of bond Cu-Cl.

For the Zn-Cl and two kind of Zn-N bonds of compound $Zn(DAT)_2Cl_2$, the BDE_{ZPE} values increase in the order N (6)-Zn < $N(4)^2$-Zn(47) < Cl-Zn, which is different from the results of bond length order $N(4)^2$-Zn < N(6)-Zn < Cl-Zn. Similarly, this phenomenon occurs in molecule $Cu(DAT)_2Cl_2$.

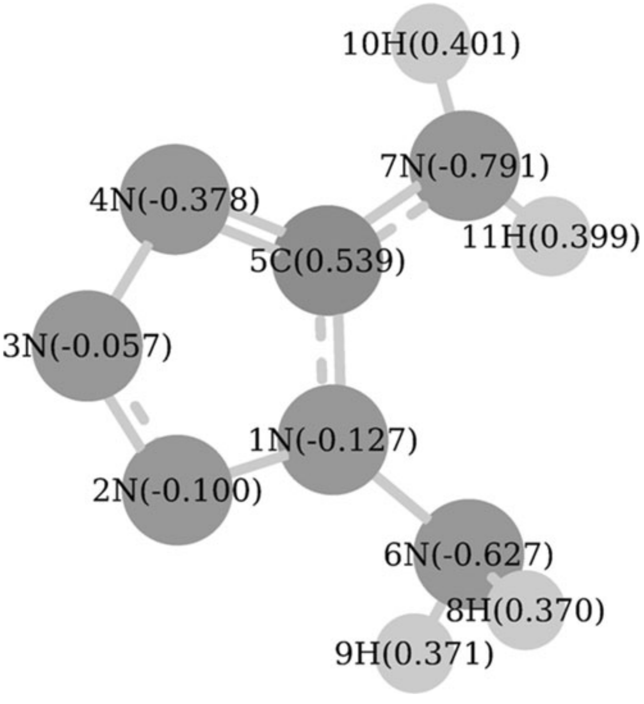

Fig. 4 NBO charges of DAT

Fundamentally, the bond energy or BDE_{ZPE} of the covalent bond between two atoms will decrease as the covalent bond lengths becoming longer. Then we can infer that MT-N coordination bonds are covalent, but the MT-Cl coordination bonds are predominantly ionic in nature. The ionic bond strength can be determined by its BDE_{ZPE}. Therefore, in a $Zn(DAT)_2Cl_2$ molecule Zn-Cl bond is relatively stable, not being concerned with the initial fission. The initial scission step of molecule $Zn(DAT)_2Cl_2$ should be the scission of the two Zn-N(6) bonds.

Li [48, 49] reported that the impact and shock sensitivities decreases as the X-NO_2 (X=C, N, O) BDE_{ZPE} enlarges for some typical energetic nitrocompounds, in which X-NO_2 bond is generally the weakest bond. Additionally, Table 5 tells that molecule $Zn(DAT)_2Cl_2$ is more insensitive than $Cu(DAT)_2Cl_2$ under impact and shock.

Detonation properties

The heat of formation (HOF) and density (ρ) (Fig. 6) were calculated by atomization scheme and using the electron cloud enclosed volume (V_{en}) discussed above, respectively.

The surface shape, size of covered volume named enclosed volume of electron cloud of molecules $Zn(DAT)_2Cl_2$ and $Cu(DAT)_2Cl_2$ are similar (Fig. 2). Gaponik et al. [20] have reported the crystal density of $Cu(DAT)_2Cl_2$, of which the isovalue is 0.0166. The crystal structures of $Zn(DAT)_2Cl_2$ and $Cu(DAT)_2Cl_2$ are almost the same, so the isovalue of $Zn(DAT)_2Cl_2$ is 0.0166, too. Hence, we got the density of $Zn(DAT)_2Cl_2$ easily by Eq. (1), 2.117 $g\cdot cm^{-3}$.

Based on the above parameters, we calculated the detonation velocity (v_D) and pressure (P_D) of TEMCs that contain Co, Cu and Zn with modified VLW code (Table 5) [44]. The corresponding results are shown in Table 6.

N-N bond always has more contribution to the heats of formation in high-nitrogen compounds [24], and the data in Table 6 show that $Cu(DAT)_2Cl_2$ and $Zn(DAT)_2Cl_2$ may possess more energies than energetic initiator BNCP. It is found that the v_D of the three compounds increases in the order $Cu(DAT)_2Cl_2$ < BNCP < $Zn(DAT)_2Cl_2$, and the value of their P_D is close. Encouragingly, the densities of $Zn(DAT)_2Cl_2$ and $Cu(DAT)_2Cl_2$ are even a little larger than that of BNCP.

Conclusions

In this paper, a detailed study on TEMCs $Cu(DAT)_2Cl_2$ and the designed molecule $Zn(DAT)_2Cl_2$ was performed by an improved theoretical method.

It is a simple and reasonable method using NBO charges to determine the possible coordination sites of molecule DAT, and this method might be suitable for prognosticating

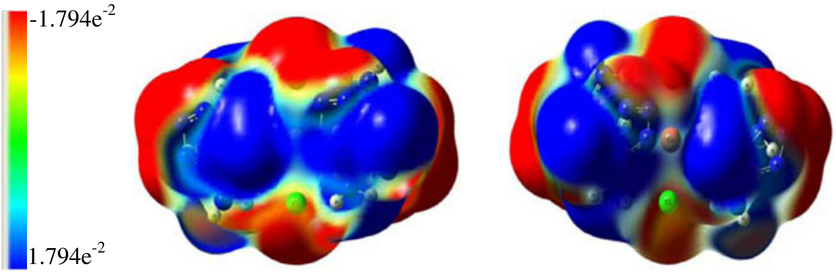

Fig. 5 The MESP of Zn(DAT)$_2$Cl$_2$ (*left*) and Cu(DAT)$_2$Cl$_2$ (*right*). (*Red* and *blue* surfaces represent electron rich and poor regions, respectively, with colors representing values between −1.794e^{-2} and 1.794e^{-2} Hartree.)

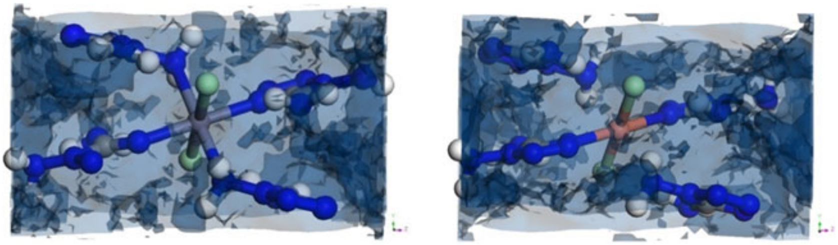

Fig. 6 Electron cloud of molecules Zn(DAT)$_2$Cl$_2$ and Cu(DAT)$_2$Cl$_2$

Table 6 The data for HOF, ρ, v_D and P_D of molecules Cu(DAT)$_2$Cl$_2$ and Zn(DAT)$_2$Cl$_2$

Compounds	HOF/(kcal·mol^{-1})	ρ/(g·cm^{-3})	v_D/(km·s^{-1})	P_D/(GPa)
Cu(DAT)$_2$Cl$_2$	67.267	2.107^a	7.773	24.948
Zn(DAT)$_2$Cl$_2$	70.475	2.117	8.325	24.709
BNCP	−167.970	2.05^b	8.030^c	26.028

a and b are from ref. [20] and [53], respectively. c: the v_D of BNCP reported by Smirnov [10] is 8.1 km·s^{-1} at a single crystal density of 1.97 g·cm^{-3}

the possible coordination sites of other kind of ligands. N-Zn and N-Cu coordination bonds are covalent, but the Zn-Cl and Cu-Cl coordination bonds are predominantly ionic in nature. The intermolecular hydrogen bonds between the networks can increase the thermal stability of the crystals of the title compounds.

The high positive heat of formation and high nitrogen content indicate a high-energy output of the title two complexes, and they may obtain more energies than energetic initiator BNCP. The v_D of the three compounds increases in the order Cu(DAT)$_2$Cl$_2$ < BNCP < Zn(DAT)$_2$Cl$_2$, and their ρ and P_D are close. These two compounds could be energetic material candidates.

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