Theoretical Studies on the Role of Guest in α-CL-20/Guest Crystals

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Abstract: The contradiction between energy and safety of explosives is better balanced by the host-guest inclusion strategy. To deeply analyze the role of small guest molecules in the host–guest system, we first investigated the intermolecular contacts of host and guest molecules through Hirshfeld surfaces, 2-D fingerprint plots and electrostatic interaction energy. We then examined the strength and nature of the intermolecular interactions between CL-20 and various small molecules in detail, using state-of-the-art quantum chemistry calculations and elaborate wavefunction analyses. Finally, we studied the effect of the small molecules on the properties of CL-20, using density functional theory (DFT). The results showed that the spatial arrangement of host and guest molecules and the interaction between host and guest molecules, such as repulsion or attraction, may depend on the properties of the guest molecules, such as polarity, oxidation, hydrogen content, etc. The insertion of H2O2, H2O, N2O, and CO2 had significant influence on the electrostatic potential (ESP), van der Waals (vdW) potential and chemical bonding of CL-20. The intermolecular interactions, electric density and crystal orbital Hamilton population (COHP) clarified and quantified the stabilization effect of different small molecules on CL-20. The insertion of the guest molecules improved the stability of CL-20 to different extents, of which H2O2 worked best.

Keywords: host-guest; intermolecular interaction; electrostatic potential; CL-20; COHP

1. Introduction

As the most widely investigated high energetic compound, hexanitrohexaazaisowurtzitane (CL-20), with typical polymorphs of α, β, γ and ε has the highest energy density [1], but it is still not widely in service due to its high sensitivity [2], phase transformations [1] and high cost. Host–guest inclusion strategy is an effective method to significantly alleviate the contradiction between high energy and low sensitivity. The development of host–guest compound explosives can solve the problems of laboriousness and risk of developing new energetic materials [3–7]. Bennion et al. [6] incorporated one solvate hydrogen peroxide (H2O2) molecule into the crystal system of anhydrous ε-CL-20, and obtained the CL-20 hydrogen peroxide solvate (CL-20/H2O2) for the first time. It had high crystallographic density (2.03 g·cm−3), high predicted detonation velocity/pressure, performed better than ε-CL-20, and had a sensitivity similar to that of ε-CL-20. Xu et al. [7] incorporated oxidizing gas molecules (N2O, CO2) into ε-CL-20 to obtain the CL-20/N2O and CL-20/CO2 complexes. CL-20/N2O exhibited a surprisingly high crystallographic density (2.038 g·cm−3 at 298 K), more thermal stability, better predicted detonation properties and lower sensitivity compared with ε-CL-20. The guest-accessible volume in α-CL-20, without being occupied by water, revealed sufficient void space to encompass some solvent molecules such as two H2O2, CO2 and N2O. Little deformation of the lattice parameters was changed after removing the water under heating/vacuum from α-CL-20 [8]. Therefore, the crystal structures of (a) CL-20, (b) CL-20/H2O2, (c) CL-20/CO2, (d) CL-20/N2O, and (e) CL-20/H2O remained isosstructural to the hydrated α-CL-20 [6,7]. A chemical diagram and molecular structure of
CL-20 are shown in Figure 1, and a planar view of the cocrystal structures are shown in Figure 2. These structures are reliable. Their original structures are the crystal structures downloaded from CCDC, and their CCDC numbers are 251409, 1495519, 771863, 1585914, and 1495521, respectively. Extensive calculation work [9,10] has demonstrated that the incorporation of small guest molecules improved the detonation performance (detonation heat, detonation pressure, detonation velocity, etc.) of the host high-energy explosive CL-20. The practical application of the host–guest explosive is always inseparable from the interaction between host and guest molecules in the system. A study of the intermolecular interaction is crucial for understanding the behavior of the complex in the actual environment and facilitating its application in practice. Meanwhile, the intermolecular interaction is the central scientific issue of energetic cocrystals [11–13]. Therefore, systematic studies on the comparison of interactions between the host–guest energetic complexes constructed by embedding different small molecules into the crystal lattice cavity of α-CL-20, are necessary. Further research devoted to summarizing the influence of guest molecules on the performance of α-CL-20 in order to explore more host–guest energetic complexes, is necessary.

Figure 1. (a) chemical diagram of CL-20, (b) molecular structure of a CL-20 molecule corresponding to the chemical diagram.

In this paper, we will explore the potential interaction between the host and guest molecules and summarize the influence of guest molecules on the host explosive. Specifically, Hirshfeld surfaces and 2-D fingerprint plots show the intermolecular contacts. First, we examine how the electrostatic interaction energy shows the strength of the intermolecular contacts. Then, we employ ESP and vdw potential to intuitively describe the electrostatic and vdw interaction characteristics of the host and guest molecules. This analysis provides us with a general understanding of the basic character of the intermolecular interaction of this species. After that, we carefully examine the COHP analysis, charge density and difference charge density of host–guest complexes; the composition of each will be useful for detailed chemical bonding analysis. This part of the research will help us grasp the chemical bonding variation of CL-20 by embedding different small molecules. Finally, we summarize which guest type has dominant influence on the host CL-20.
2. Computational Methods

The Gaussian 16 (A.03) [14] program was implemented to analyze geometry optimizations and frequency using the uB97XD exchange correlation function [15] in conjunction with the def2-TZVP basis set [16]. The process of geometry optimization is the process of obtaining reasonable structure. In order to obtain a reliable WFN file, it was converted from CIF file format. Then, Multiwfn 3.7 code, developed by one of the authors of this paper in [17], was performed to analyze the ESP, vdW potential, non-covalent interaction (NCI) map, contour map of electrostatic potential, electrostatic interaction energy, IRI and isosurface map of electron density on the basis of the optimized geometry. Visual Molecular Dynamics (VMD) software [18] was rendered to analyze isosurface maps of various real space functions based on the files exported by Multiwfn.

A freely available software, CrystalExplorer [19], was not only applied to visualize ab initio molecular ESPs mapped on Hirshfeld surfaces [20] or isosurfaces of the electron density, but was also used to calculate quantum-mechanical properties of molecules [21]. In the region of the hydrogen bonds, the isosurfaces overlap significantly, whereas Hirshfeld surfaces touch, and quite clearly demonstrate the way in which complementary electropositive (blue) and electronegative (red) regions of adjacent molecules come into contact in such an interaction [22]. The intermolecular interactions in crystals can be directly observed by electrostatic potentials mapped on Hirshfeld surfaces. The intermolecular interactions can be analyzed quantitatively and qualitatively by two-dimensional mapping [23,24] in a convenient color plot. The intermolecular contacts were explored by the points on the surface which were defined by the distances to the nearest atoms outside, \( d_{\text{e}} \), and inside, \( d_{\text{i}} \) [25]. During the theoretical investigations by CrystalExplorer, the chosen part of crystal structures was automatically selected by CrystalExplorer software from the CIF files. The chosen part of crystal structures was periodic for the crystal structures.

Bader’s QTAIM [26] method and DFT calculations with Critic2 [25] were used to investigate the intra- and inter-molecular interaction strength. The core and valence electron densities and difference charge density of each crystal were obtained from DFT calculations implemented by VASP [27]. During the theoretical investigations by VASP, the chosen part of crystal structures was selected by the nearest two neighbors. Furthermore, although LOBSTER was originally designed with interfaces to handle only wavefunctions from

Figure 2. The unit cell: (a) CL-20, (b) CL-20/H2O2, (c) CL-20/CO2, (d) CL-20/N2O, and (e) CL-20/H2O. Gray, blue, red, and white spheres stand for carbon, nitrogen, oxygen and hydrogen atoms, respectively.
while using LOBSTER, the crystal orbital Hamilton population (COHP) analysis was demonstrated and reported in [28]. LOBSTER is a multiplatform tool that is written in object-oriented C++ and parallelized using OpenMP. It employs Boost libraries [29] in addition to the highly efficient Eigen library [30].

3. Results and Discussion

3.1. The Intermolecular Contacts of Host and Guest Molecules

Usually, two interacting molecules stack in a special direction due to electrostatic attraction. The magnitude of the electrostatic attraction depends on the closer contact of the positive and negative ESPs [30,31]. From the surface minima and maxima sites (shown in Figure 3), the outermost distribution are minima of CL-20. The minima sites are evenly distributed in the extension space corresponding to O atoms of N-NO2 fragments. This demonstrates that CL-20 more easily forms H-bonds with other molecules at the minima sites. Therefore, the distribution of guest molecules is affected by the ESP-mapped molecular vdW surface. When there are no hydrogen atoms in the guest molecules, such as N2O and CO2, the distribution of host and guest molecules is very different to that of H2O and H2O2. For CO2, there is perfect linear symmetry; CO2 is arranged diagonally along the two N-O bonds, with the oxygen atom closer to the CL-20 fragment. However, the minima sites are around the O atom of CO2. Therefore, CO2 and CL-20 fragments show mutual repulsion. For N2O, the O atom is closer to the CL-20 fragment, too. The mutual repulsion causes the CL-20 to undergo large structural changes with the large deflection of one of the NO2 fragments. One minima and maxima around the O atom around N2O causes the distribution of CL-20/N2O and CL-20/CO2 to be different. The different oxidizability of H2O and H2O2 causes the different distribution of CL-20/H2O and CL-20/H2O2. The distance between the CL-20 fragment and H2O2 is closer than that of other complexes of host and guests, as shown as Figure 3.

To obtain a better understanding of the host–guest driven inclusion behavior between CL-20 and guest molecules, the intermolecular interactions [4,32] of single crystals were studied by freeware of Hirshfeld surfaces, as shown in Figure 4. In the Hirshfeld surface analysis, the red and blue areas represent the probability of close and far contact with external molecules, respectively. The red regions arranged in the oxygen and hydrogen atoms are shown in Hirshfeld surfaces. This implies the main intermolecular interactions contacts of CL-20 are focused on O and H atoms. The reaction sites of the H atom are consistent with the conclusion of Figure 3. The number of red regions (i.e., close contacts) is the same for the CL-20 fragment of the five substances. However, the sites of the red regions for the host–guest complex are distinctly different than for CL-20. The red regions around the guest molecules are much more obvious than around the host. The intensity of the red areas for guests decreases in this order: H2O2, H2O, N2O, and lastly, CO2. This demonstrates that CL-20 is much more stable after incorporating guest molecules. This conclusion is consistent with the finding that CL-20/N2O has higher thermal stability and lower impact sensitivity than CL-20 [32]. The dnorm Hirshfeld surfaces for CL-20, CL-20/N2O, CL-20/H2O, and CL-20/H2O2 resemble a whole shape. However, it is quite different for CL-20/CO2. The Hirshfeld surface is significantly different, in that it divides into two parts. The sites of the red regions for the CL-20 fragment are obviously biased to where the CO2 molecule is located. The different results may be due to the different polarity of the guest molecules.

The 2-D fingerprint plot directly demonstrates the intermolecular interactions of internal and external distances of atoms from the surface. It is possible to show the range of structures by the changes in the fingerprint plots while adding the guest into the host explosive. We applied this tool to show the intermolecular interaction variation after insertion of the guest molecules in CL-20. The graph in Figure 5 changes as different guests are embedded; there is a noticeable decrease in symmetry about the x/y diagonal in the following order: CO2, H2O, N2O, and lastly, H2O2, especially for the fingerprint of CL-20/H2O2. For pure CL-20, Figure 6 shows that intermolecular interactions are governed by O . . . O contacts. The O . . . O interactions that
usually appear in energetic crystal [33–35], can be readily understood by the internal moieties of CL-20 being dominated by the O atom. This is one of the factors that determine the high energy release of CL-20. The O atoms with high negative ESPs (shown in Figure 1) to form O...O contacts can lead to a big electrostatic repulsion. This is not conducive to the stability of CL-20. The steric in the cage and rings is also shown in the plots of IRI and RDG isosurface. The other two main intermolecular interactions are H...O and O...H contacts. The existence of hydrogen bonds is beneficial to the stability of CL-20. The O...O contacts percentage contribution to the Hirshfeld surface decreases in the order of: CL-20 (44.2%), CL-20/CO₂ (42.4%), CL-20/H₂O₂ (37.6%), CL-20/N₂O (36.8%), and CL-20/H₂O (35.9%). This implies that the repulsion in the cage and rings may decrease with the same order. The intuitive exhibition of repulsion in the cage and rings are shown in the plots of the NCI isosurface. The O...H and H...O contacts percentage contribution of CL-20/H₂O₂ is larger than for CL-20. By combining the decreasing O...O contacts and the increasing HBs, it can be inferred that CL-20/H₂O₂ is more stable than CL-20.

**Figure 3.** The surface minima and maxima: (a) CL-20, (b) CL-20/H₂O₂, (c) CL-20/CO₂, (d) CL-20/N₂O, and (e) CL-20/H₂O. Red and blue spheres represent the position of maxima and minima, respectively.
The 2-D fingerprint plot directly demonstrates the intermolecular interactions of internal and external distances of atoms from the surface. It is possible to show the range of structures by the changes in the fingerprint plots while adding the guest into the host explosive. We applied this tool to show the intermolecular interaction variation after insertion of the guest molecules in CL-20. The graph in Figure 5 changes as different guests are embedded; there is a noticeable decrease in symmetry about the x/y diagonal in the following order: CO$_2$, H$_2$O, N$_2$O, and lastly, H$_2$O$_2$, especially for the fingerprint of CL-20/H$_2$O$_2$. For pure CL-20, Figure 6 shows that intermolecular interactions are governed by O…O contacts. The O…O interactions that usually appear in energetic crystal [33–35], can be readily understood by the internal moieties of CL-20 being dominated by the O atom. This is one of the factors that determine the high energy release of CL-20. The O atoms with high negative ESPs (shown in Figure 1) to form O…O contacts can lead to a big electrostatic repulsion. This is not conducive to the stability of CL-20. The steric in the cage and rings is also shown in the plots of IRI and RDG isosurface. The other two main intermolecular interactions are H…O and O…H contacts. The existence of hydrogen bonds is beneficial to the stability of CL-20. The O…O contacts percentage contribution to the Hirshfeld surface decreases in the order of: CL-20 (44.2%), CL-20/CO$_2$ (42.4%), CL-20/H$_2$O$_2$ (37.6%), CL-20/N$_2$O (36.8%), and CL-20/H$_2$O (35.9%). This implies that the repulsion in the cage and rings may decrease with the same order. The intuitive exhibition of repulsion in the cage and rings are shown in the plots of the NCI isosurface. The O…H and H…O contacts percentage contribution of CL-20/H$_2$O$_2$ is larger than for CL-20. By combining the decreasing O…O contacts and the increasing HBs, it can be inferred that CL-20/H$_2$O$_2$ is more stable than CL-20.

The inter-fragment interaction between all the defined fragments (one fragment is the host CL-20, the other fragment is one of the small guest molecules) can easily be recognized by the electrostatic interaction energy. The electrostatic interaction energies between guest molecules and the selected atoms of CL-20 are shown in Table 1, with a calculation of which are closer to the guest molecules. The most important contribution to the attraction is the electrostatic interaction of the O … H, O … N and O … C contacts; this result is easy to understand since O is the acceptor atom of these contacts. However, even though there were rejections between O … O contacts and O … N contacts, the fragments between
N$_2$O, H$_2$O$_2$, H$_2$O and CL-20 attract each other. This contributes greatly to the sum of the electrostatic effect with binding (−0.14, −8.93, −0.11 kJ·mol$^{-1}$). Meanwhile, the attraction between H$_2$O$_2$ and CL-20 is very obvious and cannot be ignored, as the binding energy is much less than 0. This may be because of the different electrostatic potential (ESP) and van der Waals (vdW) potential of CL-20/H$_2$O$_2$ contrary to the other complexes. However, the mutual repulsion of the fragment CO$_2$ and CL-20 contributes greatly to the sum of the electrostatic effect without binding (0.03 kJ·mol$^{-1}$). Therefore, the CL-20 fragment combined with N$_2$O, H$_2$O$_2$, H$_2$O fragments may be a whole molecule. The CL-20 fragment with CO$_2$ may be two fragments. This conclusion confirms the two parts of the Hirshfeld surface for CL-20/CO$_2$, as shown in Figure 4. The two different kinds of interaction between CL-20/N$_2$O, CL-20/H$_2$O$_2$, CL-20/H$_2$O and CL-20/CO$_2$ may be caused by the polarity of the guest molecules.

![Figure 6](image-url)

**Figure 6.** The individual atomic contact percentage contribution to the Hirshfeld surface of CL-20 and its complexes: (a) CL-20, (b) CL-20/H$_2$O$_2$, (c) CL-20/CO$_2$, (d) CL-20/N$_2$O, and (e) CL-20/H$_2$O.

**Table 1.** The electrostatic interaction energy (kJ·mol$^{-1}$) between the two fragments of four host–guest explosives.

| Electrostatic Interaction Energy | CL-20/N$_2$O | CL-20/H$_2$O$_2$ | CL-20/H$_2$O | CL-20/CO$_2$ |
|---------------------------------|-------------|----------------|-------------|-------------|
| Guest . . . H                   | −0.21       | −1.55          | −0.45       | −0.11       |
| Guest . . . H                   | −0.23       | −1.20          | −0.47       | −0.07       |
| Guest . . . H                   | −0.23       | −3.77          | −0.29       | −0.09       |
| Guest . . . H                   | −0.28       | −0.29          | −0.07       |
| Guest . . . C                   | −0.13       | −1.14          | −0.27       | −0.07       |
| Guest . . . C                   | −0.14       | −0.80          | −0.24       | −0.04       |
| Guest . . . C                   | −0.13       | −1.44          | −0.26       | −0.05       |
| Guest . . . C                   | −0.18       | −0.29          | −0.07       |
| Guest . . . N                   | −1.4        | −6.20          | −1.47       | −0.34       |
| Guest . . . N                   | −0.96       | −5.08          | −1.42       | −0.28       |
| Guest . . . O                   | 0.49        | 5.41           | 1.01        | 0.13        |
| Guest . . . O                   | 0.52        | 1.76           | 0.93        | 0.18        |
| Guest . . . O                   | 0.83        | −0.65          | 0.9         | 0.33        |
| Guest . . . O                   | 0.7         | 1.81           | 0.84        | 0.38        |
| Guest . . . N                   | 0.34        | 2.62           | 0.42        | 0.08        |
| Guest . . . N                   | 0.31        | 1.36           | 0.43        | 0.13        |
| Guest . . . CL-20               | −0.14       | −8.93          | −0.11       | 0.03        |
3.2. Electrostatic and vdW Interaction Characteristics of Host and Guest Molecules

The electrostatic potential (ESP) on the molecular vdW surface was used to study and predict intermolecular interaction, for example, the information of the close contact site, structure property and special hydrogen bonding [36–38], which is usually employed to study the molecular packing in cocrystals [39]. Therefore, it is very useful to investigate the important interaction between the host explosive and small guest molecules. The ESP-mapped vdW surface, in addition to the surface extrema of CL-20 and its host–guest complexes, are shown in Figure 7, and their surface areas are plotted as shown in Figure 8.

![Figure 7](image_url)

**Figure 7.** ESP—mapped molecular vdW surface of: (a) CL-20, (b) CL-20/H2O2, (c) CL-20/CO2, (d) CL-20/N2O, and (e) CL-20/H2O. The unit is in kcal·mol⁻¹. Surface local minima and maxima of ESP are represented as green and orange spheres, respectively. The global minimum and maximum are labeled by blue and red colors, respectively.

![Figure 8](image_url)

**Figure 8.** Surface area in each ESP range on the vdW surface of: (a) CL-20, (b) CL-20/H2O2, (c) CL-20/CO2, (d) CL-20/N2O, and (e) CL-20/H2O.
It can be seen that oxygen atoms of NO$_2$ have negative surface potential, while C-H and cage have positive surface potential as demonstrated in Figure 7. The O of CO$_2$ is closer to CL-20 and possesses negative ESP (−13.7 kcal·mol$^{-1}$). The ESP of the CL-20 fragment, which is close to CO$_2$, is also negative (−19.54, −18.87 kcal·mol$^{-1}$). This determines that the two molecules are mutually exclusive. Of the two negative ESP for O atoms of N$_2$O, one (−16.18 kcal·mol$^{-1}$) is inter-attraction with positive ESP (44.63, 43.74 kcal·mol$^{-1}$) of CL-20. The other (−19.38 kcal·mol$^{-1}$) is mutually repulsive with negative ESP (−18.08, −19.42 kcal·mol$^{-1}$) of CL-20. The equilibrium of the two forces determines the distribution of the CL-20 fragments and N$_2$O. The two hydrogen atoms possess positive ESP (46.83 and 47.31 kcal·mol$^{-1}$), corresponding with the negative ESP (−14.46 and −19.68 kcal·mol$^{-1}$) of the CL-20 fragment. The H . . . CL-20 contacts are of mutual affinity. Between the two negative ESP, there are many higher positive ESP relatively far from H$_2$O. The H$_2$O . . . CL-20 contacts are mutually repulsive. The balance of the two forces determines the distribution of the CL-20 fragments and H$_2$O. In the configuration of CL-20/H$_2$O$_2$, the negative surface potential of CL-20 (−25.40 kcal·mol$^{-1}$) overlaps with the positive surface potential of H in H$_2$O$_2$ (43.8 and 46.02 kcal·mol$^{-1}$), indicating that noncovalent CL-20 . . . H$_2$O$_2$ bonds are formed at the same time. The interaction between CL-20 and H$_2$O is bigger than other host and guest molecules. The values of the electrostatic interaction energy between CL-20 and the guest molecules are shown in Table 1.

Figure 8 illustrates the characteristic of ESP distribution of CL-20 and the additional guest parts in the CL-20 unit cell, respectively. For ESP distribution of CL-20, the positive part mainly arises from the positively charged C-H carbon atoms. The remarkable positive and negative ESP value are small areas, corresponding to the regions closed to the global ESP minimum (−18.5 kcal·mol$^{-1}$) and maximum (83.5 kcal·mol$^{-1}$), respectively. The whole CL-20 surface partition is affected by the different guest molecules. For the CL-20, the vdW surface area is 310.16 Å$^2$. By comparing the experimental data, the proportion of ESP distribution of the CL-20 fragment occupies, in order: 81.4%, 84.1%, 86.6%, and 90.7% of the overall surface for CL-20/N$_2$O, CL-20/CO$_2$, CL-20/H$_2$O, and CL-20/H$_2$O$_2$, respectively. It shows that the H$_2$O$_2$ guest has the least effect on the surface area of host–guest cell. CL-20/N$_2$O has the biggest surface area. This may be caused by the polarity of whole host–guest complex. The greater the polarity, the greater the ESP surface area. It can be seen from the graph that there is a large portion of the CL-20 molecular surface having a small ESP value, namely, from −15.5 to 8.5 kcal·mol$^{-1}$. The main distribution area widens from −18.57 to 11.15, −19.32 to 10.96, −15.5 to 14.8, and −17.54 to 27.04 kcal·mol$^{-1}$, for CL-20/H$_2$O$_2$, CL-20/H$_2$O, CL-20/CO$_2$, and CL-20/N$_2$O, respectively. The ESP surface area proportion of the CL-20 fragment can determine the degree of broadening order of the main distribution area. When the H$_2$O fragment embeds into the cell of CL-20, the ESP distribution on the vdW surface fluctuates most dramatically. The higher negative ESP value of CL-20/H$_2$O is the largest, while the extreme values vary little for the other complexes, compared with CL-20. This indicates that CL-20/H$_2$O more easily forms H-bonds with other molecules than CL-20.

From the graph for CL-20 (Figure 9a), it is clear that the C and H atoms form bonds. The C-H fragments are overall positively charged because they largely intersect solid contour lines of the vdW surface close to the two C-H fragments. This shows that the C-H fragments are surrounded by positive value lines, and suggests that the C-H segments are more susceptible to electrophilic reactions that are more stable when they receive hydron. While embedding different small molecules into the crystal lattice cavity of α-CL-20, the symmetry of the contour map of electrostatic potential is broken, and the contour lines become chaotic. This may be because the symmetry of CL-20 is broken. This shows that all host–guest complexes contribute to electrophilic reactions in the same manner as that of CL-20. However, the reaction sites may be a little changeable for the different intersect regions. The combining capacity with hydron, decided by the maximum of energy data, is in the following order: CL-20/H$_2$O (94.54 eV), CL-20 (78.14 eV), CL-20/CO$_2$ (55.68 eV), CL-20/N$_2$O (48.55 eV), and CL-20/H$_2$O$_2$ (11.50 eV). This implies that CL-20/H$_2$O$_2$ may be the most stable complex, while the CL-20/H$_2$O may be the liveliest complex.
Figure 9. Contour map of electrostatic potential of CL-20 and its host–guest complex: (a) CL-20, (b) CL-20/H₂O₂, (c) CL-20/CO₂, (d) CL-20/N₂O, and (e) CL-20/H₂O. The bold blue line corresponds to the vdW surface (isosurface of electron density = 0.001 a.u., as defined by R. F. W. Bader). The solid and dashed lines represent the region having positive and negative values of ESP, respectively. The isovalue starts at ± 0.001 a.u., and doubles at each step.

The color-filled NCI isosurface not only demonstrates where weak interaction occurs, but is also an intuitive presentation of their interaction—such as repulsion or attraction—and their magnitude. We can identify different types of regions by simply examining their colors. Recalling the color scale bar shown previously in Figure 10A, more blue implies a stronger attractive interaction. The elliptical slab between the oxygen and hydrogen atoms shows green color in Figure 10, so we can conclude that there exists a hydrogen bond, but not a very strong one. The yellow circle demonstrates the vdW interaction region, which shows that the electron density in this region is low. Obviously, the regions at the center of the cage and rings correspond to strong steric interaction, since they are filled by red. This result explains the relatively low stability of CL-20. The configuration of the CL-20 fragment changes significantly in the host–guest complex, due to the appearance of the vdW interaction region between the two NO₂ fragments. The configuration caused by the repulsion of guest molecules and NO₂ prepares enough space to accommodate guest molecules. The red color becomes lighter and the shape becomes thinner at the center of the cage in the host–guest complex. This demonstrates that the cage of CL-20 fragments in the host–guest complex is more stable than the CL-20. This conclusion is consistent with the finding that the CL-20/N₂O has higher thermal stability and lower impact sensitivity than CL-20 [39,40].
Figure 10. Plots of NCI isosurface for CL-20 and its host—guest complexes: (a) CL-20, (b) CL-20/H$_2$O$_2$, (c) CL-20/CO$_2$, (d) CL-20/N$_2$O, and (e) CL-20/H$_2$O. The surfaces between the host and guest molecules correspond to the isosurface of RDG (isovalue = 0.5) mapped by sign ($\lambda_2$)$\rho$ function. The color scale is given in a.u.: (A) the interactions in the cage structure are highlighted, (B) the interactions between host and guest molecules are highlighted.

Figure 10B focuses on demonstrating the interaction of the host and guest molecules. The isosurface values for CL-20/N$_2$O, CL-20/H$_2$O, and CL-20/H$_2$O$_2$ are 0.9 a.u. except for CL-20/CO$_2$, which is 1.1 a.u. The interaction regions of H$_2$O . . . CL-20, N$_2$O . . . CL-20, and CO$_2$ . . . CL-20 contacts are green color, so the hydrogen bonds are not very strong. The strength of the interaction decreases in the order of: CL-20/H$_2$O, CL-20/N$_2$O, and CL-20/CO$_2$, in the area of the interaction region. The interaction between CO$_2$ and CL-20 is relatively small. These results are consistent with the electrostatic interaction energy between CO$_2$ and CL-20. The interaction regions of H$_2$O$_2$ . . . CL-20 contacts are bluish on the ends and red in the middle. The hydrogen bond and the repulsion between oxygen atoms are very strong. This strong hydrogen bond of H$_2$O$_2$ . . . CL-20 contacts may be the
The polarities of CL-20 and its host–guest complexes are rather high, since their MPIs (NCI isosurface). It further explains that the CL-20/H2O2 is the special existence for the other complexes. The addition of H2O2 has little effect on the intramolecular reaction of CL-20. However, the electron density of CL-20/H2O, CL-20/CO2, and CL-20/N2O are rarer than of CL-20 when λ2 < 0. This displays that the addition of H2O, CO2, and N2O weakens the intramolecular forces and intermolecular hydrogen bonds. Table 1 demonstrates that the summation of H…Guest electrostatic interaction energy of CL-20/H2O, CL-20/CO2 and CL-20/N2O is much less than one H…H2O2 hydrogen bond. Table 1 demonstrates that the summation of H…Guest electrostatic interaction energy of CL-20/H2O, CL-20/CO2 and CL-20/N2O is much less than one H…H2O2 (14.95 kcal·mol−1) electrostatic interaction energy. It also shows that the addition of H2O, CO2, and N2O weakens the intermolecular hydrogen bonds.

Figure 11. Plots of IRI for CL-20 and its host—guest complex: (a) CL-20, (b) CL-20/H2O2, (c) CL-20/CO2, (d) CL-20/N2O, and (e) CL-20/H2O.

A comparison of molecular polarity index values reveals that the guest molecules with greater polarity such as CL-20/H2O (19.56 kcal·mol−1), CL-20/N2O (19.53 kcal·mol−1) and CL-20/H2O2 (19.5 kcal·mol−1) correspond to the macropolar host–guest complex more than CL-20 (18.61 kcal·mol−1). CL-20/CO2 (14.95 kcal·mol−1) has the smallest polarity. The polarities of CL-20 and its host–guest complexes are rather high, since their MPIs are higher than benzene (8.4 kcal·mol−1) [42], which possesses the common unsaturated hydrocarbons as determined by experimental chemists. This further implies that the strength of the electrostatic interaction between the CL-20 and its host–guest complex should be fairly strong. The stronger the electrostatic interaction is, the more stable the explosive is. The results are consistent with the conclusion shown by the color-filled NCI isosurface.
Owing to the relatively low polarity of CL-20/CO₂, the vdW interaction [43] of CL-20/CO₂ is likely to be very important with regard to its electrostatic interaction in intermolecular complexation. In Figure 12, the green isosurface represents the region where vdW is negative. The guest molecules tend to be attracted to the green region due to the driven force of dispersion attraction. The region close to the nuclei is fully enclosed by blue isosurface, indicating that the exchange repulsion potential dominates the vdW potential in this area. The surfaces of the vdW potential show that CL-20/H₂O₂ is a whole, while other host–guest complexes are comprised of two parts. This contributes to the closer distance between CL-20 and H₂O₂. This is also intuitively shown in the color-filled NCI isosurface. It further explains that the CL-20/H₂O₂ is the special existence for the other complex.

3.3. Effect on the Chemical Bonding of CL-20 by the Small Molecules

The electronic structure, shown in Figure 13, and the charge, change [44] before and after embedding different small molecules into the crystal lattice cavity of α-CL-20. The yellow isosurface (0.001 a.u.) represents the region in which the electron density of the bonds increases. As shown in Figure 13a, it is obvious that electron density shifts from C-H fragments toward N-NO₂ fragments to strengthen the bonding energy. The electrons mainly accumulate in the branch chain of CL-20. The electronegativity of O atoms of the nitro branch chain is larger than that of N and C atoms, causing the electron cloud density of the entire cage structure to be biased towards O atoms, thus presenting greater electronegativity. The electronegativity of N atoms is smaller than that of O atoms, and the electronegativity of N atoms is larger than that of the cage structure. This demonstrates that the N-NO₂ bonds are more active than the N-O bonds. This is consistent with the conclusion that CL-20 has only one distinct initial decomposition channel homolysis of the N-NO₂ bond. The cages of other atoms are electropositive. The positive electricity compared with the smaller distance between atoms by the cage structure, further intensifies the mutually repulsive force of the cage structure. This is an important factor in determining the instability of CL-20. The result corresponds with the incidental phase transformations [45,46], and the cage collapse with the C-N bonds rupture [47]. Table 2 lists the charge density of each atom for CL-20 and its complexes. The variation tendency of charge density between CL-20/CO₂ and CL-20/N₂O are similar, while it is slightly different to CL-20. The variation tendency of charge density between CL-20/H₂O and CL-20/H₂O₂ is similar. However, the variation trend is very different from CL-20. This indicates that CO₂ and N₂O have little effect on the charge density of CL-20, while H₂O and H₂O₂ have a larger effect on the charge.
density of CL-20. This difference may depend on whether the guest molecule contains hydrogen atoms.

Figure 13. The electric charge density of CL-20 and its complexes: (a) CL-20, (b) CL-20/H2O2, (c) CL-20/CO2, (d) CL-20/N2O, and (e) CL-20/H2O, respectively.

Table 2. The charge of all atoms for CL-20 and its complexes.

|       | CL-20 | CL-20/H2O2 | CL-20/CO2 | CL-20/N2O | CL-20/H2O |
|-------|-------|------------|-----------|------------|-----------|
| C1    | 3.439943 | 3.39528    | 3.365282  | 3.415394   | 3.484355  |
| C2    | 3.368974 | 3.347578   | 3.463434  | 3.414919   | 3.389329  |
| C3    | 3.407468 | 3.389311   | 3.438538  | 3.37998    | 3.440836  |
| C4    | 3.361728 | 3.364322   | 3.42262   | 3.44343    | 3.464925  |
| C5    | 3.426331 | 3.465616   | 3.465766  | 3.414552   | 3.449965  |
| C6    | 3.466851 | 3.392609   | 3.49393   | 3.406848   | 3.448265  |
| H1    | 0.760157 | 0.773847   | 0.779039  | 0.804121   | 0.769744  |
| H2    | 0.764535 | 0.816269   | 0.72438   | 0.778757   | 0.782522  |
| H3    | 0.764828 | 0.764591   | 0.727955  | 0.785294   | 0.767634  |
| H4    | 0.788069 | 0.769692   | 0.76251   | 0.753908   | 0.70013   |
| H5    | 0.735678 | 0.757301   | 0.74393   | 0.773186   | 0.784896  |
| H6    | 0.774061 | 0.812159   | 0.735494  | 0.79133    | 0.76359   |
| N1    | 4.30006  | 5.658855   | 5.674066  | 4.356636   | 5.641745  |
| N2    | 5.73423  | 5.769231   | 4.295426  | 5.628674   | 5.661261  |
| N3    | 4.292966 | 5.749727   | 5.641763  | 5.628986   | 5.688769  |
| N4    | 5.691062 | 5.615677   | 4.311871  | 4.260681   | 5.666997  |
| N5    | 4.307686 | 5.61475    | 5.724673  | 5.690055   | 5.638395  |
| N6    | 5.671315 | 5.708823   | 4.291829  | 4.263904   | 5.622085  |
| N7    | 4.335934 | 4.317027   | 5.75138   | 5.672504   | 4.344943  |
| N8    | 5.758303 | 4.307445   | 4.228027  | 4.313575   | 4.308732  |
| N9    | 4.273575 | 4.302678   | 5.659884  | 5.631423   | 4.276512  |
| N10   | 5.641856 | 4.291919   | 4.290824  | 4.28659    | 4.314033  |
| N11   | 4.276822 | 4.279109   | 5.63803   | 5.749158   | 4.29891   |
| N12   | 5.640089 | 4.222286   | 4.324952  | 4.282773   | 4.288023  |
| O1    | 6.420255 | 6.447034   | 6.427327  | 6.423941   | 6.370973  |
| O2    | 6.404339 | 6.413201   | 6.425237  | 6.379549   | 6.403641  |
| O3    | 6.442006 | 6.401898   | 6.422331  | 6.415355   | 6.399926  |
| O4    | 6.425998 | 6.396192   | 6.400269  | 6.441002   | 6.428866  |
| O5    | 6.448879 | 6.408842   | 6.423134  | 6.443255   | 6.428065  |
| O6    | 6.39755  | 6.432817   | 6.437646  | 6.439187   | 6.442918  |
1.6 Å, the value of their -COHP is positive, which shows that the intermolecular interactions of the two NO fragments close to H2O2 is remarkable. The value of -COHP decreases according to the N-O area below 0, the more bonds there are. The charge density variation of the two NO fragments close to H2O2 is remarkable. The O atom adjacent to the H atom of H2O2 loses electrons. Therefore, the distance between the H2O2 and CL-20 is decided by the balance of two forces. For the N2O implant in CL-20, the charge change of the two NO fragments close to H2O is small. The O atom adjacent to the N atom of N2O loses electrons. Meanwhile, the O atom of N2O adjacent to the O of NO2 loses electrons, however, the interaction is very small. This demonstrates that the distance between N2O and CL-20 is a little further than that of CL-20/H2O2 and CL-20/H2O. For the CO2 incorporated in CL-20, the electrons of CL-20 show little change. Only the O atoms of CO2 obtain electrons from the C atoms of CO2. The electrostatic interaction between CO2 and CL-20 is unchanged, which results in a large distance, as also shown in Figures 4 and 10. As a result, the charge density of CL-20 changes obviously with the H2O and H2O2 insertions, although the charge density of CL-20 changes little for the N2O and CO2 insertions. The results also indicate that the distribution of the electrons transferred to the CL-20 is determined by different degrees due to the different guests. This demonstrates that the charge density variation is decided by the hydrogen contained by, and the oxidability of, guest molecules.

The COHP technique can be qualitative and correctly describes negative (i.e., bonding) and positive (i.e., antibonding) contributions [48,49] of chemical bonding with band-structure energy, as shown in Figure 15. The larger the value of the area above 0 minus the area below 0, the more bonds there are. The value of -COHP decreases according to the N-O of NO2, N-N2O2, C-N and C-C, as shown in Table 3. This demonstrates the cage structure of CL-20 is made more stable by embedding H2O2 and H2O. Therefore, the electrostatic interaction between the host and guest molecules is enhanced, which results in a decrease in the distance, and an increased intermolecular interaction. This is consistent with the charge density presented in Table 2. For the H2O implant in CL-20, the charge density variation of the two NO fragments close to H2O is remarkable. The O atom adjacent to the H atom of H2O loses electrons. However, the O atom of H2O rejects the O of NO2. Therefore, the distance between the H2O and CL-20 is decided by the balance of two forces. For the N2O implant in CL-20, the charge change of the two NO fragments close to H2O is small. The O atom adjacent to the N atom of N2O loses electrons. Meanwhile, the O atom of N2O adjacent to the O of NO2 loses electrons, however, the interaction is very small. This demonstrates that the distance between N2O and CL-20 is a little further than that of CL-20/H2O2 and CL-20/H2O. For the CO2 incorporated in CL-20, the electrons of CL-20 show little change. Only the O atoms of CO2 obtain electrons from the C atoms of CO2. The electrostatic interaction between CO2 and CL-20 is unchanged, which results in a large distance, as also shown in Figures 4 and 10. As a result, the charge density of CL-20 changes obviously with the H2O and H2O2 insertions, although the charge density of CL-20 changes little for the N2O and CO2 insertions. The results also indicate that the distribution of the electrons transferred to the CL-20 is determined by different degrees due to the different guests. This demonstrates that the charge density variation is decided by the hydrogen contained by, and the oxidability of, guest molecules.

The differential charge densities of CL-20 and its complexes are shown in Figure 14. For the H2O2 embedded in CL-20, the charge density variation of CL-20 is more obvious than for the other complexes. The charge density variation of the three NO2 fragments close to H2O2 is remarkable. The one NO2 fragment away from the inserted H2O2 obtains more electrons than the two NO2 fragments close to the H2O2. The second type is branched chain bonds such as C-H bonds, N-N bonds and N-O bonds. For CL-20/2H2O2, the +COHP of C-C bonds is significantly higher. It is a little higher for CL-20/H2O. However, it is lower relative to CL-20/CO2 and CL-20/N2O. The +COHP of C-N bonds is substantially higher for CL-20/2H2O2. It is a little higher for CL-20/H2O. However, it is lower relative to CL-20/CO2 and CL-20/N2O. The variation tendency of COHP demonstrates that the cage structure of CL-20 is made more stable by embedding H2O2 and H2O. However, the cage structure of CL-20 is made more unstable by embedding CO2 and N2O. The +COHP of C-H bonds is larger than of CL-20. The increase for CL-20/2H2O2 is significant. It shows that C-H bonds are more stable after adding guest molecules. For H2O2, CO2, N2O and H2O embedded into the

|          | CL-20   | CL-20/H2O2 | CL-20/CO2 | CL-20/N2O | CL-20/H2O |
|----------|---------|------------|-----------|-----------|-----------|
| O7       | 6.397592| 6.456496   | 6.437232  | 6.432066  | 6.447627  |
| O8       | 6.383578| 6.406194   | 6.444439  | 6.415191  | 6.393018  |
| O9       | 6.407534| 6.391632   | 6.419992  | 6.427163  | 6.410837  |
| O10      | 6.452038| 6.439611   | 6.408803  | 6.415240  | 6.419222  |
| O11      | 6.418675| 6.489760   | 6.393027  | 6.431183  | 6.442122  |
| O12      | 6.41958 | 6.441443   | 6.404066  | 6.401798  | 6.435030  |
crystal lattice cavity of $\alpha$-CL-20, the -COHPs of N-O bonds and N-N bonds are smaller than for CL-20. This shows that branched chains may be made much livelier by embedding small molecules. These results are inconsistent with those in the literature. However, it does suggest that guest molecules containing hydrogen contribute more to the stability of CL-20.

**Figure 14.** The differential charge density of CL-20 and its complexes: (a) CL-20/H$_2$O$_2$, (b) CL-20/CO$_2$, (c) CL-20/H$_2$O, and (d) CL-20/N$_2$O, respectively. The isosurface value is set to 0.006 e·Å$^{-3}$. Yellow represents charge accumulation.

**Figure 15.** The -COHP curves for the CL-20 interactions of CL-20 and its complexes: (a) C-H bonds, (b) C-C bonds, (c) C-N bonds, (d) N-N bonds, and (e) N-O bonds, respectively. In the -COHP curves, the positive and negative signs represent bonding and antibonding states, respectively. The thick trendline corresponds to the actual concentration data of the corresponding matching color.
The electrostatic interaction characteristics of host and guest molecules shows that the bonding analysis of the high-energy explosive CL-20 and the new host–guest explosives with other complexes. The surfaces of van der Waals (vdW) potential shows that other complex; CL-20/H appears as a whole, while other host–guest complex consists of two 22 is biggest, while CL-20/H 22 is the most stable complex compared O. The main findings and conclusions are summarized as follows:

1. The d\text{norm} Hirshfeld surfaces, 2-D fingerprint plot and individual atomic contact percentage contribution demonstrate that the cage of CL-20 fragments in host–guest complexes are more stable than CL-20. The electrostatic interaction energy shows that CL-20/H\textsubscript{2}O\textsubscript{2} possesses stronger hydrogen bonds and stronger mutual attraction between host and guest molecules than other complexes. The specific distribution of host and guest molecules are affected by the polarity and oxidizability of the guest molecules;

2. The electrostatic interaction characteristics of host and guest molecules shows that overlapping surface potential only occurs for CL-20/H\textsubscript{2}O\textsubscript{2}. The interaction between CL-20 and H\textsubscript{2}O\textsubscript{2} is biggest, while CL-20/H\textsubscript{2}O\textsubscript{2} is the most stable complex compared with other complexes. The surfaces of van der Waals (vdW) potential shows that CL-20/H\textsubscript{2}O\textsubscript{2} appears as a whole, while other host–guest complex consists of two parts. The potentials demonstrate that CL-20/H\textsubscript{2}O\textsubscript{2} is the special existence for the other complex;

Table 3. The ICOHP between two atoms for CL-20 and its complexes.

|       | CL-20 | CL-20/H\textsubscript{2}O\textsubscript{2} | CL-20/CO\textsubscript{2} | CL-20/N\textsubscript{2}O | CL-20/H\textsubscript{2}O\textsubscript{2} |
|-------|-------|-------------------------------------------|-----------------------------|-----------------------------|-------------------------------------------|
| C2    | 0.0002| -8.21658                                 | -0.00173                    | -0.00057                    | 0.0002                                    |
| C1    | -0.0025| -8.03599                                 | 0.00198                     | -0.0002                     | 0.0116                                    |
| C3    | -6.7622| -8.14678                                 | -0.04313                    | -0.01217                    | -6.6075                                   |
| C4    | -0.0005| -9.51721                                 | -0.00181                    | -0.0003                     | -0.0121                                   |
| C5    | -0.0019| -9.27181                                 | -0.00451                    | -0.0019                     | -0.0140                                   |
| C6    | -0.0037| -9.59336                                 | -0.00488                    | -0.00008                    | -0.0163                                   |
| C10   | -0.0131| -9.69842                                 | -0.01563                    | -0.00046                    | -0.0138                                   |
| C4    | -0.0183| -9.79839                                 | -0.01508                    | -0.00517                    | -0.0156                                   |
| C2    | -0.0176| -9.83962                                 | -0.01586                    | -0.00556                    | -0.0154                                   |
| C6    | -0.0123| -9.96269                                 | -0.01587                    | -0.00344                    | -0.0268                                   |
| C3    | -0.0025| -10.05424                                | -0.0182                     | -0.04103                    | 0.0168                                    |
| C6    | -0.0202| -10.20592                                | -0.02711                    | -0.00554                    | -0.0278                                   |
| C1    | -9.58089| -10.20256                                | -0.03043                    | -0.00211                    | -9.6602                                   |
| C2    | -9.77474| -10.59034                                | -9.53927                    | -0.09988                    | -9.7123                                   |
| C1    | -10.18768| -10.55467                                | -10.04402                   | -0.12441                    | -10.0431                                   |
| C7    | 0.0039 | -6.82756                                 | -0.00003                    | 0.00352                     | 0.00254                                   |
| H9    | 0.00039| -6.79854                                 | -0.00024                    | -0.02047                    | 0.00284                                   |
| H11   | 0.00094| -7.0202                                 | -0.0017                     | -0.02405                    | -0.02669                                   |
| H1    | -0.0436| -6.84098                                 | -8.09852                    | -0.0435                     | -0.03322                                   |
| H3    | 0.00244| -6.83071                                 | -7.98601                    | -0.46923                    | 0.01673                                   |
| H5    | -0.00919| -6.8202                                 | -8.1083                     | -0.46346                    | -7.9553                                   |
| N12   | -9.65004| -9.25005                                | -9.54528                    | -0.00024                    | -0.00058                                   |
| N10   | -9.80733| -9.95989                                 | -9.54889                    | -0.00002                    | 0.00034                                   |
| N2    | -10.25476| -9.99392                                | -9.97115                    | -0.00565                    | -0.00456                                   |
| N8    | -10.43611| -10.66563                               | -10.11909                   | -0.01187                    | -0.00033                                   |
| N6    | -10.92593| -11.20556                               | -10.81519                   | -0.4354                     | -0.00171                                   |
| N4    | -11.03219| -11.40287                               | -11.25665                   | -0.4642                     | 0.00082                                   |
| N5    | -16.25353| -15.98383                               | -16.24132                   | 0.00001                     | -9.41873                                   |
| N7    | -16.5398| -16.29451                               | -16.47698                   | 0.00006                     | -9.81729                                   |
| N3    | -16.50557| -16.88862                               | -16.47518                   | -0.04298                    | -9.78804                                   |
| N9    | -16.61515| -16.88697                               | -16.73727                   | -10.6239                    | -10.36198                                   |
| N11   | -16.6889| -16.9825                                 | -16.59197                   | -10.69822                   | -10.91247                                   |
| N1    | -16.65992| -17.23416                               | -16.77997                   | -20.88737                   | -11.55274                                   |

4. Conclusions

We conducted a systematic and in-depth theoretical exploration and comparison of the intermolecular contacts, intermolecular interaction characteristics and chemical bonding analysis of the high-energy explosive CL-20 and the new host–guest explosives CL-20/H\textsubscript{2}O\textsubscript{2}, CL-20/H\textsubscript{2}O, CL-20/CO\textsubscript{2} and CL-20/N\textsubscript{2}O. The main findings and conclusions are summarized as follows:

1. The d\text{norm} Hirshfeld surfaces, 2-D fingerprint plot and individual atomic contact percentage contribution demonstrate that the cage of CL-20 fragments in host–guest complexes are more stable than CL-20. The electrostatic interaction energy shows that CL-20/H\textsubscript{2}O\textsubscript{2} possesses stronger hydrogen bonds and stronger mutual attraction between host and guest molecules than other complexes. The specific distribution of host and guest molecules are affected by the polarity and oxidizability of the guest molecules;

2. The electrostatic interaction characteristics of host and guest molecules shows that overlapping surface potential only occurs for CL-20/H\textsubscript{2}O\textsubscript{2}. The interaction between CL-20 and H\textsubscript{2}O\textsubscript{2} is biggest, while CL-20/H\textsubscript{2}O\textsubscript{2} is the most stable complex compared with other complexes. The surfaces of van der Waals (vdW) potential shows that CL-20/H\textsubscript{2}O\textsubscript{2} appears as a whole, while other host–guest complex consists of two parts. The potentials demonstrate that CL-20/H\textsubscript{2}O\textsubscript{2} is the special existence for the other complex;
(3) The charge density of CL-20 changes obviously with H$_2$O and H$_2$O$_2$ insertion, although the charge of CL-20 changes little with N$_2$O and CO$_2$ insertion. The variation tendency of COHP demonstrates that the cage structure of CL-20 is made more stable by embedding H$_2$O and H$_2$O$_2$. However, the phenomenon is reversed by embedding CO$_2$ and N$_2$O. The charge density variation and stability of the host–guest complex is affected by the hydrogen content of the guest molecules.

The results of this study revealed that the guest H$_2$O$_2$ small molecule played a certain stable role for CL-20. For the synthesis of new energetic materials with host–guest inclusion strategy, we investigated new guest molecules by referencing properties such as geometry configuration, oxidability, polarity and hydrogen content of H$_2$O$_2$. Our results provide fundamental insight into the roles of guest molecules in host–guest crystals and may be helpful for the formation of new host–guest energetic materials by incorporating appropriate species of small molecules into crystal lattice voids.

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**References**

1. Nielsen, A.T.; Chafin, A.P.; Christian, S.L.; Moore, D.W.; Nadler, M.P.; Nissan, R.A.; Flippen-Anderson, J.L. Synthesis of polyazapolycyclic caged polynitramines. *Tetrahedron* 1998, 54, 11793–11812. [CrossRef]
2. Simpson, R.L.; Urtiliew, P.A.; Ornellas, D.L.; Moody, G.L.; Scribner, K.J.; Hoffman, D.M. CL-20 Performance Exceeds that of HMX and its Sensitivity is Moderate. *Propell. Explos. Pyrot.* 1997, 22, 249–255. [CrossRef]
3. Van der Heijden, A.E.; Bouma, R.H. Crystallization and Characterization of RDX, HMX, and CL-20. *Cryst. Growth Des.* 2004, 4, 999–1007. [CrossRef]
4. Navasardyan, M.A.; Kuz’mina, L.G.; Churakov, A.V. Unusual isomorphism in crystals of organic solvates with hydrazine and water. *CrystEngComm* 2019, 21, 5693–5698. [CrossRef]
5. Wang, Y.; Song, S.; Huang, C.; Qi, X.; Wang, K.; Liu, Y.; Zhang, Q. Hunting for advanced high-energy-density materials with well-balanced energy and safety through an energetic host–guest inclusion strategy. *J. Mater. Chem. A* 2019, 7, 19248–19257. [CrossRef]
6. Vuppuluri, V.S.; Bennion, J.C.; Wiscons, R.A.; Gunduz, L.E.; Matzger, A.J.; Son, S.F. Detonation velocity measurement of a hydrogen peroxide solvate of CL-20. *Propell. Explos. Pyrot.* 2019, 44, 313–318. [CrossRef]
7. Bennion, J.C.; Chowdhury, N.; Kampf, J.W.; Matzger, A.J. Hydrogen peroxide solvates of 2, 4, 6, 8, 10, 12-hexanitro-2, 4, 6, 8, 10, 12-hexaazaisowurtzitane. *Angew. Chem. Int. Ed.* 2016, 128, 13312–13315. [CrossRef]
8. Xu, J.; Zheng, S.; Huang, S.; Tian, Y.; Liu, Y.; Zhang, H.; Sun, J. Host–guest energetic materials constructed by incorporating oxidizing gas molecules into an organic lattice cavity toward achieving highly-energetic and low-sensitivity performance. *Chem. Commun.* 2019, 55, 909–912. [CrossRef]
9. Pu, L.; Xu, J.J.; Liu, X.F.; Sun, J. Investigation on the thermal expansion of four polymorphs of crystalline CL-20. *J. Energ. Mater.* 2016, 34, 205–215. [CrossRef]
10. Xiao, Y.; Chen, L.; Geng, D.; Yang, K.; Lu, J.; Wu, J. A quantum-based molecular dynamics study of the ICM-102/HNO$_3$ host-guest reaction at high temperatures. *Phys. Chem. Chem. Phys.* 2020, 22, 27002–27012. [CrossRef]
11. Xiao, Y.; Chen, L.; Geng, D.; Yang, K.; Lu, J.; Wu, J.; Yu, B. Reaction mechanism of embedding oxidizing small molecules in energetic materials to improve the energy by reactive molecular dynamics simulations. *J. Phys. Chem. C* 2019, 123, 29144–29154. [CrossRef]
12. Liu, G.; Wei, S.H.; Zhang, C. Review of the intermolecular interactions in energetic molecular cocystals. *Cryst. Growth Des.* 2020, 20, 7063–7079. [CrossRef]
13. Zhao, X.; Huang, S.; Liu, Y.; Li, J.; Zhu, W. Effects of noncovalent interactions on the impact sensitivity of HNS-based cocryystals: A DFT study. *Cryst. Growth Des.* 2018, 19, 756–767. [CrossRef]
14. Ji, J.; Zhu, W. Theoretical studies on the role of each component in benzotriifuroxan/2, 4, 6-trinitrotoluene co-crystal. *Chem. Phys. Lett.* 2020, 753, 137608. [CrossRef]

15. Steinberg, S.; Dronskowski, R. The crystal orbital Hamilton population (COHP) method as a tool to visualize and analyze chemical bonding in intermetallic compounds. *Crystals* 2018, 8, 225. [CrossRef]

16. Chai, J.D.; Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections. *Phys. Chem. Chem. Phys.* 2008, 10, 6615–6620. [CrossRef]

17. Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* 2005, 7, 3297–3305. [CrossRef]

18. Lu, T.; Chen, F. Multifinw: A multifunctional wavefunction analyzer. *J. Comput. Chem.* 2012, 33, 580–592. [CrossRef]

19. Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual molecular dynamics. *J. Mol. Graph. Mod.* 1996, 14, 33–38. [CrossRef]

20. Wolff, S.K.; Grimwood, D.J.; McKinnon, J.J.; Jayatilaka, D.; Spackman, M.A. *CrystalExplorer*, 2.1; University of Western Australia: Perth, Australia, 2007.

21. Spackman, M.A.; Jayatilaka, D. Hirshfeld surface analysis. *CrystEngComm* 2009, 11, 19–32. [CrossRef]

22. Spackman, P.R.; Turner, M.J.; McKinnon, J.J.; Wolff, S.K.; Grimwood, D.J.; Jayatilaka, D.; Spackman, M.A. *CrystalExplorer*: A program for Hirshfeld surface analysis, visualization and quantitative analysis of molecular crystals. *J. Appl. Cryst.* 2021, 54, 1006–1011. [CrossRef] [PubMed]

23. Wood, P.A.; McKinnon, J.J.; Parsons, S.; Pidcock, E.; Spackman, M.A. Analysis of the compression of molecular crystal structures using Hirshfeld surfaces. *CrystEngComm* 2008, 10, 368–376. [CrossRef]

24. Spackman, M.A.; McKinnon, J.J. Fingerprinting intermolecular interactions in molecular crystals. *CrystEngComm* 2002, 4, 378–392. [CrossRef]

25. McKinnon, J.J.; Spackman, M.A.; Mitchell, A.S. Novel tools for visualizing and exploring intermolecular interactions in molecular crystals. *Acta Crystallogr. B* 2004, 60, 627–668. [CrossRef]

26. McKinnon, J.J.; Fabbiani, F.P.; Spackman, M.A. Comparison of polymorphic molecular crystal structures through Hirshfeld surface analysis. *Cryst. Growth Des.* 2007, 7, 755–769. [CrossRef]

27. McKinnon, J.J.; Jayatilaka, D.; Spackman, M.A. Towards quantitative analysis of intermolecular interactions with Hirshfeld surfaces. *Chem. Commun.* 2007, 37, 3814–3816. [CrossRef]

28. Richard, F.; Bader, R. *Atoms in Molecules: A Quantum Theory*; Clarendon Press: Oxford, UK, 1990.

29. Otero-de-la-Roza, A.; Blanco, M.A.; Pendás, A.M.; Luañá, V. Critical: A new program for the topological analysis of solid-state electron densities. *Comput. Phys. Commun.* 2009, 180, 157–166. [CrossRef]

30. Otero-de-la-Roza, A.; Johnson, E.R.; Luañá, V. Critical2: A program for real-space analysis of quantum chemical interactions in solids. *Comput. Phys. Commun.* 2014, 185, 1007–1018. [CrossRef]

31. Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B* 1993, 47, 558. [CrossRef]

32. Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* 1996, 6, 15–50. [CrossRef]

33. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* 1999, 54, 11169. [PubMed]

34. Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* 1999, 59, 1758. [CrossRef]

35. Nelson, R.; Konze, P.M.; Dronskowski, R. First-principles chemical bonding study of manganese carbodiimide, MnNCO, as compared to manganese oxide, MnO. *J. Phys. Chem. A* 2017, 121, 7778–7786. [CrossRef] [PubMed]

36. Nelson, R.; Ertural, C.; George, J.; Deringer, V.L.; Hautier, G.; Dronskowski, R. LOBSTER: Local orbital projections, atomic charges, and chemical-bonding analysis from projector-augmented-wave-based density-functional theory. *J. Comput. Chem.* 2020, 41, 1931–1940. [CrossRef] [PubMed]

37. Rivera, R. Boost c++ Libraries. 2013. Available online: http://www.boost.org/ (accessed on 13 April 2022).

38. Guennebaud, G.; Jacob, B. Eigen. 2010. Available online: http://eigen.tuxfamily.org (accessed on 3 June 2013).

39. Frisch, M.J. *GAUSSIAN16*; Revision A. 03; Gaussian Inc.: Wallingford, CT, USA, 2016.

40. Ma, Y.; Meng, L.; Li, H.; Zhang, C. Enhancing intermolecular interactions and their anisotropy to build low-impact-sensitivity energetic crystals. *CrystEngComm* 2017, 19, 3145–3155. [CrossRef]

41. Gelalcha, F.G.; Schulze, B.; Lönnecke, P. 3, 3, 6, 6-Tetramethyl-1, 2, 4, 5-tetroxane: A twinned crystal structure. *Acta Crystallogr. C* 2004, 60, o180–o182. [CrossRef] [PubMed]

42. Zhang, C.; Xue, X.; Cao, Y.; Zhou, J.; Zhang, A.; Li, H.; Gao, T. Toward low-sensitive and high-energetic co-crystal II: Structural, electronic and energetic features of CL-20 polymorphs and the observed CL-20-based energetic-energetic co-crystals. *CrystEngComm* 2014, 16, 5905–5916. [CrossRef]

43. Ma, Y.; Zhang, A.; Xue, X.; Jiang, D.; Zhu, Y.; Zhang, C. Crystal packing of impact-sensitive high-energy explosives. *Cryst. Growth Des.* 2014, 14, 6101–6114. [CrossRef]
46. Lu, T.; Manzetti, S. Wavefunction and reactivity study of benzo [a] pyrene diol epoxide and its enantiomeric forms. *Struct. Chem.* 2014, 25, 1521–1533. [CrossRef]

47. Wei, X.; Ma, Y.; Long, X.; Zhang, C. A strategy developed from the observed energetic-energetic cocrystals of BTF: Cocrystallizing and stabilizing energetic hydrogen-free molecules with hydrogenous energetic coformer molecules. *CrystEngComm* 2015, 17, 7150–7159. [CrossRef]

48. Contreras-García, J.; Yang, W.; Johnson, E.R. Analysis of hydrogen-bond interaction potentials from the electron density: Integration of noncovalent interaction regions. *J. Phys. Chem. A* 2011, 115, 12983–12990. [CrossRef]

49. De Silva, P.; Corminboeuf, C. Simultaneous visualization of covalent and noncovalent interactions using regions of density overlap. *J. Chem. Theory Comput.* 2014, 10, 3745–3756. [CrossRef] [PubMed]