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Metal–Organic Frameworks (MOFs) as Safer, Structurally Reinforced Energetics

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Abstract: Second-generation cobalt and zinc coordination architectures were obtained through efforts to stabilize extremely sensitive and energetic transition-metal hydrazine perchlorate ionic polymers. Partial ligand substitution by the tridentate hydrazinecarboxylate anion afforded polymeric 2D-sheet structures never before observed for energetic materials. Carefully bal-

anced reaction conditions allowed the retention of the noncoordinating perchlorate anion in the presence of a strongly chelating hydrazinecarboxylate

Keywords: coordination polymers • crystal engineering • density functional calculations • energetic materials • metal–organic frameworks

ligand. High-quality X-ray single-crystal structure determination revealed that the metal coordination preferences lead to different structural motifs and energetic properties, despite the nearly isoformulaic nature of the two compounds. Energetic tests indicate highly decreased sensitivity and DFT calculations suggest a high explosive performance for these remarkable structures.

Introduction

A pressing goal of current research is the design and development of greener energetic materials^[1] with special emphasis on the replacement of the lead-based primary explosives^[2] that have widespread use in military, civilian, and commercial applications. To function as a primary explosive, a particular combination of energy content and detonation sensitivity is required. Herein, we disclose the crystal engineering of zinc- and cobalt-based, 2D metal–organic frameworks (MOFs) with solid-state structures that afford exemplary performance and properties. Although research concerning MOFs traditionally targets applications requiring porosity,^[3] such as heterogeneous catalysis, gas storage, filtering, and sensing, many of the precepts of MOF design can be readily applied to the preparation of improved metal-based energetic compounds, for which high density is desirable. Specifically, the ability to utilize the structural reinforcement available in multidimensional architectures can afford advanced energetic materials that would otherwise be unstable or unattainable.

Recently, we reported new ionic polymeric energetic materials with tremendous energetic output.^[4] These Ni and Co hydrazine–perchlorate (NHP and CHP, respectively) 1D coordination polymers provide the energy of conventional secondary explosives but avoid the use of the heavy metals still common in primary energetics. Unfortunately, the high sensitivity of NHP and CHP may preclude their commercial use. Beyond their energetic properties, the NHP and CHP crystal structures demonstrated the overlooked potential of hydrazine as a ligand for solid-state architectures. They were the first crystal structures with hydrazine as the sole inner-sphere ligand and form one-dimensional chains with just one bridging hydrazine molecule defining the backbone of the coordination polymer (Figure 1 a). The low rigidity characteristic of such linear polymeric structures combined with fairly weak Ni– or Co–nitrogen bonds and high hydrazine to metal ratio yielded highly sensitive compounds, especially in the case of NHP. Continuing our efforts to explore the structural potential of hydrazine as a ligand for coordination polymers and the preparation of improved energetic materials in tandem, we present herein second-generation, metal-based, nitrogen-rich architectures, for which structural modification of the ligand results in layered structures with a considerable reduction of sensitivity.

Results and Discussion

Design and synthetic considerations: Examination of the NHP and CHP poly-metalhydrazine perchlorate^[4] structures reveals several directions for possible structural modifications. The easiest modification, anion substitution, is not viable since the choice is restricted to oxidizing nitrate or perchlorate anions. Both Ni and Co hydrazine nitrates have

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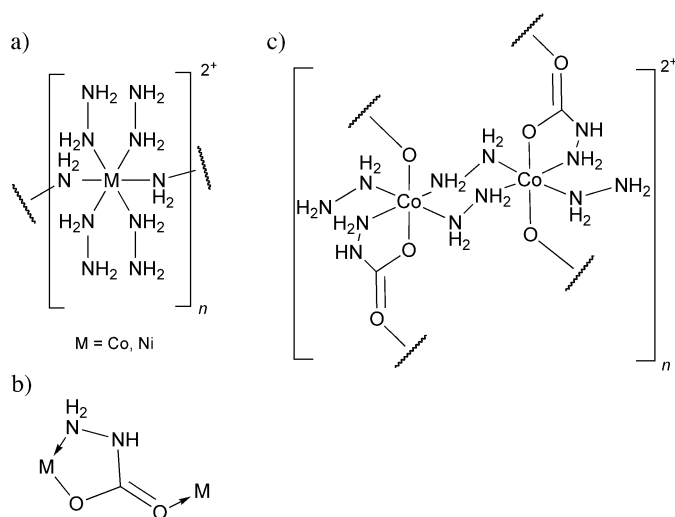


Figure 1. a) Schematic of NHP and CHP motif. b) The binding mode of hydrazinecarboxylate. c) Schematic showing the cobalt dimers.

previously been prepared and yielded materials of only modest energetic performance,^[5] which indicates that the use of nitrate instead of perchlorate will sacrifice oxidizing capacity too severely. Azides, which are commonly employed in energetic materials (EMs),^[6] will not allow the most energy-efficient utilization of the oxidizable hydrazine scaffold due to their nonoxidizing nature. Theoretically, the metal core of the coordination polymers can be substituted by other transition metals, thus changing the electronic distribution in the complex, or alternatively the energetic ligand itself can be modified. The shortcoming of metal substitution lies in the fact that only a limited number of combinations are practical or even possible. A fairly small number of metals prefer nitrogen-based coordination, as opposed to oxophilic metals, which will readily hydrolyze to form more favorable M–O bonds. The choice is further narrowed by the desire to avoid the use of toxic heavy metals or expensive noble metals. Finally, the ligand modification can only be carried out in such a way as to allow the overall preservation of the polymeric backbone, which confers structural and chemical stability.

Hydrazine is almost ideal as a ligand for energetic coordination polymers owing to its bidentate nature, exclusively gaseous decomposition products, and the absence of any oxidizable carbon, which would reduce the oxygen balance of the final EM. However, the previously prepared NHP and CHP proved highly sensitive and extremely powerful—a dangerous combination—hence the need for another ligand that would somewhat attenuate their energetic properties. Consequently, our requirement for hydrazine modification is to retain the polydentate nature of the ligand while avoiding alkyl or aryl substituents on the hydrazine moiety. The spontaneous and unanticipated reaction of hydrazine with atmospheric carbon dioxide furnished an excellent candidate: hydrazinecarboxylic acid.

Hydrazine is known to react with carbon dioxide to yield hydrazinecarboxylic acid.^[7] The hydrazinecarboxylate anion

can serve as a bi- or tridentate ligand and consequently can be used for the construction of coordination polymers.^[8] Due to its chelating nature, however, it often forms stable, monomeric bis-^[9] or tris-hydrazinecarboxylate^[7,10] complexes with transition metals. Nevertheless, crystallographic studies demonstrate that the coordination chemistry of hydrazinecarboxylate is much richer than for unsubstituted hydrazine because it can coordinate to the metal center in at least three different ways.^[7] The arrangement of interest to this investigation results from the interaction of the carbonyl oxygen electron pair with the neighboring metal center which results in the linkage of two metal centers by hydrazine carboxylate (Figure 1b). The carboxylate carbon atom serves as a latent source of carbon dioxide, decreasing the energy content and density and desensitizing the compound. The combination of the oxidizing perchlorate anion, the highly energetic bidentate hydrazine ligand, and the stabilizing and bridging hydrazinecarboxylate chelate appears to fully satisfy the design requirements for practical, stabilized polymeric energetic compounds.

In retrospect, the foremost challenge in successfully synthesizing the above design elements arises from the need to preserve the noncoordinating perchlorate anion in the presence of the competitive, chelating hydrazinecarboxylate anion. This became clear following synthetic attempts that involved treating a metal perchlorate/hydrazine solution with CO₂-saturated hydrazine; this approach merely led to precipitation of metal hydrazinecarboxylate complexes. In fact, similar methods have been previously employed to obtain monomeric transition metal hydrazinecarboxylates.^[10] Furthermore, examination of crystal structures reported in the Cambridge Structural Database that include a metal bonded to a hydrazinecarboxylate reveals that no structures have been reported in which a metal-hydrazinecarboxylate crystallizes alongside another ancillary anion. In order to incorporate the perchlorate ion in the structure, the concentration ratio of perchlorate/hydrazinecarboxylate must be greatly increased. Instead of saturating hydrazine with carbon dioxide, simple absorption of atmospheric carbon dioxide by solutions of either cobalt or zinc perchlorate in water/hydrazine as the solvent provides the correct balance. On the order of hours for cobalt and tens of hours for zinc, crystalline energetic products formed; single-crystal X-ray diffraction identified these as Co- and Zn- hydrazine hydrazinecarboxylate perchlorate complexes ([Co₂(N₂H₄)₄-(N₂H₃CO₂)₂][ClO₄]₂·H₂O (CHHP) and [Zn₂(N₂H₄)₃-(N₂H₃CO₂)₂][ClO₄]₂·H₂O (ZnHHP)).

Crystallography: Crystallographic data for CHHP and ZnHHP are summarized in Table 1 to facilitate comparison. CHHP crystallizes in the monoclinic *P*2₁/*c* space group with half a formula unit per asymmetric unit and two formula units per unit cell. CHHP forms a sheet polymer in the solid state composed of distorted octahedral metal centers with mixed coordination spheres. The sheets lie parallel to the crystallographic *bc* plane and stack along the crystallographic *a* axis with layers of perchlorate anions between the

Table 1. Crystallographic data collection and refinement summary.

	CHHP ^[a]	ZnHHP ^[b]
color and shape	orange plates	colorless needles
M_r	613.09	593.92
ρ_{calcd} [g cm ⁻³]	2.000	2.117
crystal system	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a [Å]	9.7762(9)	7.8541(6)
b [Å]	11.3848(11)	9.3723(7)
c [Å]	10.0190(9)	13.2825(10)
α [°]	90	90.228(1)
β [°]	114.054(1)	92.174(1)
γ [°]	90	107.492(1)
V [Å ³]	1018.28(16)	931.73(12)
Z	2	2
resolution [°]	26.37	26.73
R_{merge}	0.0265	0.0176
completeness to θ_{max} [%]	100	99.4
redundancy	5.06	2.68
reflms (collected/unique)	10805/2085	10534/3925
data/restraints/parameters	2085/230/14	3925/325/21
goodness of fit on F^2	1.050	1.060
R_1 ^[c] (R_1 all data)	0.0221 (0.0247)	0.0321 (0.0361)
wR_2 ^[c] (wR_2 all data)	0.0586 (0.0604)	0.0835 (0.0861)
max, min peaks [e ⁻ Å ⁻³]	0.65, -0.31	1.14, -0.74

[a] $[\text{Co}_2(\text{N}_2\text{H}_4)_4(\text{N}_2\text{H}_3\text{CO}_2)_2][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$.

[b] $[\text{Zn}_2(\text{N}_2\text{H}_4)_3(\text{N}_2\text{H}_3\text{CO}_2)_2][\text{ClO}_4]_2 \cdot \text{H}_2\text{O}$. [c] $I > 2\sigma(I)$.

sheets. Each metal bears three hydrazine ligands. One ligand coordinates in a terminal monodentate mode and two others bridge to a second metal center to form cobalt dimers (shown schematically in Figure 1c). Each metal also bears two hydrazinecarboxylate ligands, one of which chelates the cobalt through the terminal nitrogen and one oxygen and the other hydrazinecarboxylate coordinates to the metal center in a monodentate mode through an oxygen atom. Hence, every hydrazinecarboxylate ligand is tridentate (Figure 1b) and bridges two metal centers parallel to the c axis. The resulting sheet is a 2D network of mixed-ligand cobalt dimers (Figure 2a). The perchlorate anion is disordered almost equally over two positions with both components contributing to the hydrogen-bond network holding the sheets together.

ZnHHP crystallizes as “starburst” arrays of needles in a triclinic $P\bar{1}$ space group with one formula unit per asymmetric unit and two formula units per unit cell. Although ZnHHP has a similar formula to CHHP, and is also comprised of alternating sheets of metal coordination polymer and perchlorate anions, it shows different and highly varied coordination chemistry at the zinc metal center. ZnHHP forms a 2D polymeric sheet, which is comprised of three different zinc coordination environments (Figure 2b). Portions of the 2D sheet polymer appear to be arranged in a “ladder” motif. The “rungs” are composed of octahedral zinc centers, each with two monodentate, terminal hydrazine ligands that are *trans* to each other and two bridging hydrazinecarboxylate ligands, which are also in a mutually *trans* arrangement. The “arms” of the ladder consist of two additional zinc centers that form a network of shared hydrazine and hydrazinecarboxylate ligands. One zinc center has a dis-

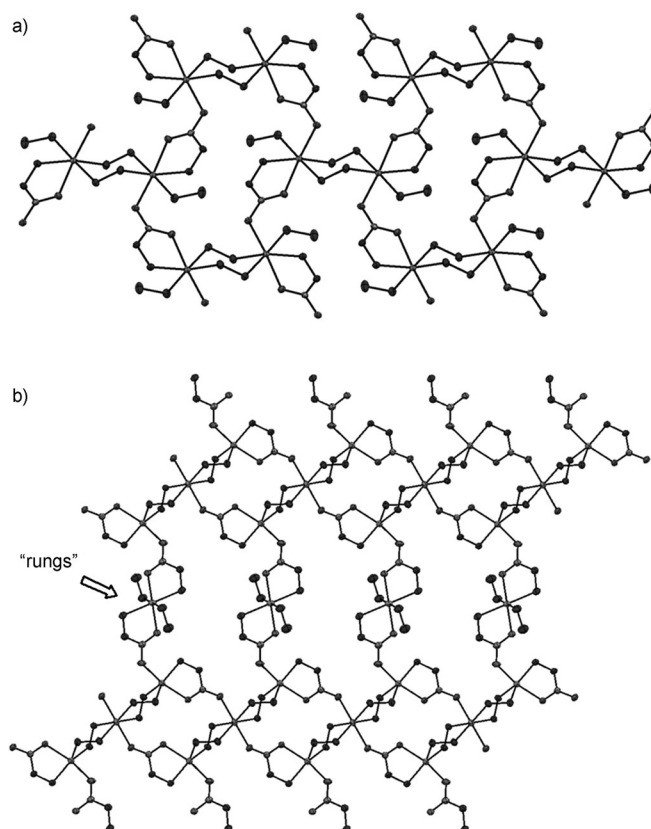


Figure 2. a) Partial packing diagram of CHHP showing the sheet structure parallel to the bc plane. b) Partial packing diagram of a ZnHHP sheet showing the ladder motif. In both graphics, perchlorate anions and cocrystallized water have been omitted for clarity.

torted-square-pyramidal coordination sphere in which the base of the pyramid is defined by bonds to two hydrazine ligands and one bidentate hydrazinecarboxylate ligand and the apical bond of the pyramid joins this zinc center to the rung of the ladder structure. The final zinc center is octahedral with four equatorial hydrazine ligands and two axial bonds to hydrazinecarboxylate oxygen atoms. As in the case of CHHP, every hydrazinecarboxylate is tridentate and binds to two metal centers.

The nickel analogue of these compounds was not obtained due to the high sensitivity of NHP, solutions of which can be explosive. The series cannot be extended to copper due to the fact that copper perchlorate reacts vigorously with hydrazine at room temperature.

Sensitivity evaluations: The sensitivity of CHHP and ZnHHP assessed qualitatively by means of a homemade drophammer apparatus^[11] and spark tests shows a marked decrease compared with previously studied NHP and CHP (Table 2). CHHP can still be initiated by a spark, but ZnHHP is insensitive to such stimulus. CHHP detonates on exposure to flame whereas ZnHHP deflagrates. The differential scanning calorimetry (DSC) plots show single exotherms corresponding to decomposition with no phase changes observed; the decomposition temperatures of

Table 2. Energetic Sensitivities.

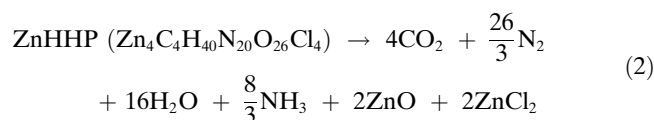
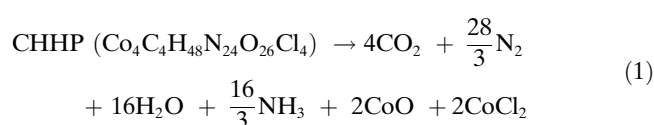
Material	Drophammer response [cm], [kg]	ESD ^[a] sensitivity	Flame sensitivity	Decomposition temperature [°C]
CHHP	30, 2.5	detonates	detonates	231
ZnHHP	50, 5	insensitive	deflagrates	293
CHP	20, 2.5	detonates	detonates	194
PETN	42, 2.5	insensitive	burns	141 (melts)

[a] Electrostatic discharge.

CHHP and ZnHHP (231 and 293 °C, respectively) are much higher than that of CHP (194 °C). The higher stability of CHHP and ZnHHP observed relative to NHP and CHP prompted us to perform computational studies on these compounds to assess whether these complexes had retained sufficient energy content to serve effectively as energetic materials.

Computational assessment: To estimate the heat of detonation (ΔH_{det}) of these two new explosives and see how they compare with the ΔH_{det} values for common energetic materials we adopted the methodology recently employed for NHP and CHP.^[4] In this method we use density functional theory (DFT) to compute the energy of detonation ($\Delta E_{\text{DFT,det}}$; the difference in total energy between a crystal unit cell of the energetic material and the sum of the total energy of the products), from which ΔH_{det} is estimated by using a linear correlation developed from known ΔH_{det} data for eleven commonly used high explosives.^[4] As in ref. [4], the DFT calculations for CHHP and ZnHHP were performed with the code DMol3 under 3D periodic boundary conditions employing the Monkhorst–Pack multiple k -point sampling of the Brillouin zone and the Perdew–Becke–Ezerhoff (PBE) exchange–correlation function. Given large uncertainties in the positions of hydrogen atoms in the XRD-determined structures, the H-atom positions were optimized by DFT, and the heavy atoms were kept constrained in their XRD-assigned positions. To represent the inherent disorder in the position of the ClO_4^- ions and water molecules in the CHHP unit cell, we considered all possible distinct combinations of positions and determined the average value of ΔH_{det} . However, the variation in ΔH_{det} due to variation in the positions of ClO_4^- and water was found to be small, less than 1.5 %, and does not change any of the conclusions below.

For both CHHP and ZnHHP, water, nitrogen, carbon dioxide, and ammonia were assumed to be the final products of decomposition of the organic part of the framework and the formation of a mixture of metal oxides and chlorides was assumed to be governed by the deficiency of oxygen. The complete decomposition reactions considered for CHHP and ZnHHP are described by Equations (1) and (2).



All non-metal-containing products, including water, were treated as a gas. The resultant heat of detonation values (Figure 3) indicate that the newly prepared 2D MOFs are

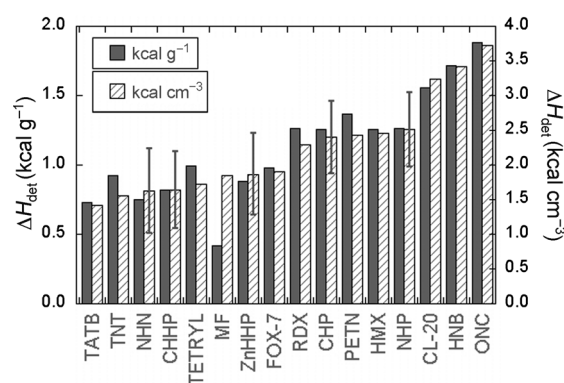


Figure 3. Bar chart representation of the literature ΔH_{det} values for eleven common explosive materials including triaminotrinitrobenzene (TATB), trinitrotoluene (TNT), 2,4,6-trinitrophenylmethylnitramine (tetryl), mercury fulminate (MF), 1,1-diamino-2,2-dinitroethylene (FOX-7), cyclotrimethylenetrinitramine (RDX), pentaerythritol tetranitrate (PETN), cyclotetramethylenetetranitramine (HMX), hexanitrohexaazaisowurtzitane (CL-20), hexanitrobenzene (HNB), and octanitrocubane (ONC). Previously reported values for CHP, NHP, and NHN, along with the predicted ΔH_{det} values for CHHP and ZnHHP are also shown. Error bars correspond to the 95 % statistical-confidence level for these values.

modestly more energetic than nickel hydrazine nitrate (NHN), the ionic polymer of reference from the previous study, while possessing considerably lower energetic output than reported for CHP and NHP. Such a decrease in heats of detonation is expected due to the lower perchlorate load and significantly increased structural stabilization coming from the chelating hydrazinecarboxylate anion and a network of hydrogen bonds between the parallel sheets of compounds. Nevertheless, CHHP and ZnHHP still outperform traditional metal-based energetics by delivering energetic output on the order of magnitude of common organic secondary explosives such as TNT, tetryl, and FOX-7, while displaying moderate sensitivities, appropriate for convenient handling and intentional initiation.

Conclusion

Herein, we have advanced the idea that the design of metal-based energetics should be approached intellectually as has been the case for traditional metal–organic frameworks. The goal of such designs is to obtain multidimensional structures that possess the desired physical (density) and chemical properties (energetic output and sensitivity). As examples of

this suggested paradigm in energetic materials engineering, two novel, highly energetic MOFs, CHHP and ZnHHP, were synthesized and characterized. Both materials are composed of alternating layers of structurally stabilized metal-organic fuel and oxidizing perchlorate anions. Both structures are held together by mixed hydrazine-hydrazinecarboxylate bridges as opposed to the previously reported linear polymers, NHP and CHP, which are bridged by a single hydrazine ligand. As a result of these structural modifications, CHHP and ZnHHP possess much milder sensitivity profiles, but retain higher energy content than typical metal-based explosives, comparable instead to those of conventional organic secondary explosives. Consequently, these species are excellent candidates for replacing heavy-metal primers such as lead azide.

The crystal structures represent the first example of the co-existence of the chelating hydrazinecarboxylate anion with any other anion in the solid state. Careful preparative techniques allow preservation of the necessary oxidizing anion even in the presence of a very competitive anionic chelating ligand. The strategy of allowing the slow reaction of hydrazine with atmospheric CO₂ provides an elegant route to new mixed-ligand systems. Examination of the CHHP and ZnHHP coordination modes demonstrates the rich structural variety that can be accessed, even in compounds that utilize the same ligands and coordination modes (e.g., in which hydrazine is a *trans*-bridging or monodentate ligand and hydrazinecarboxylate is always tridentate). Notably, slight structural differences between the two compounds amount to a change of approximately 15% in predicted energetic output. Hence, the choice of metal in MOF-based energetic materials directs and determines the solid-state structure and ultimately the energetic properties of the material.

Experimental Section

Hazard warning and safety precautions: The prepared metal hydrazine hydrazinecarboxylate perchlorate complexes are very powerful energetic substances, capable of initiation by impact, friction, electric spark, heating, or open flame. The utmost care and strict adherence to safety protocols (such as use of face shields, Kevlar gloves, and materials least capable of static discharge) are necessary at all times. The starting materials also pose a danger because hydrazine hydrate is a known carcinogen and perchlorates are powerful oxidants.

Materials and methods: Cobalt perchlorate hexahydrate and zinc perchlorate hexahydrate were obtained from Alfa Aesar and hydrazine hydrate (64%) from Acros Organics. All reagents were used without further purification. Water was deionized. Elemental analysis was performed on a PerkinElmer 2400 Series II CHNS/O Analyzer. X-ray diffraction data were obtained on a Bruker Smart Apex II single-crystal X-ray diffractometer at 150 K by using MoK α radiation with a wavelength of 0.71073 Å. A multi scan absorption correction (SADABS) was applied. Structures were solved by direct methods and refined with SHELX-97 software.^[12] All hydrogen atoms were located from the electron density map and refined by using distance restraints. CCDC-892692 (CHHP) and CCDC-892693 (ZnHHP) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The

Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

CHHP: Cobalt(II) perchlorate hexahydrate was dissolved in water/hydrazine hydrate and allowed to crystallize uncovered under ambient conditions. Elemental analysis calcd (%) for Co₂C₂N₁₂H₂₂Cl₂O₁₂ (595.04): C 4.04, N 28.25, H 3.73; found: C 4.31, N 28.13, H 3.39.

ZnHHP: Zinc(II) perchlorate hexahydrate was dissolved in water/hydrazine hydrate and allowed to crystallize uncovered under ambient conditions. Elemental analysis calcd (%) for Zn₂C₂N₁₀H₂₀Cl₂O₁₃ (593.91): C 4.04, N 23.61, H 3.37; found: C 4.06, N 23.40, H 3.30.

Drophammer and spark tests: Sensitivity data was obtained by use of a homemade drophammer.^[11] The instrument consists of a metal bar to which various weights can be attached. The bar is held at a user-specified height by an electromagnet; when the electromagnet is switched off, the bar and the weight will fall upon a flat-metal surface that holds the compound of interest. Thus the weight attached to the bar and the height from which it falls can be controlled, which allows the impact sensitivity of a given compound to be determined. The values for CHHP and ZnHHP are given alongside those for CHP, which were reported earlier^[4] and for reference, the impact sensitivity of pentaerythritol tetranitrate (PETN) as determined on the same apparatus.^[11] Electric spark test was performed by using a High Frequency Generator, Model BD-10AS Electro-Technic Products, at 115 V and 0.35 A.

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