Ionic Polymers as a New Structural Motif for High-Energy-Density Materials

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S *Supporting Information*

ABSTRACT: Energetic materials have been used for nearly two centuries in military affairs and to cut labor costs and expedite laborious processes in mining, tunneling, construction, demolition, and agriculture, making a tremendous contribution to the world economy. Yet there has been little advancement in the development of altogether new energetic motifs despite long-standing research efforts to develop superior materials. We report the discovery of new energetic compounds of exceptionally high energy content and novel polymeric structure which avoid the use of lead and mercury salts common in conventional primary explosives. Laboratory tests indicate the remarkable performance of these Ni- and Co-based energetic materials, while DFT calculations indicate that these are possibly the most powerful metal-based energetic materials known to date, with heats of detonation comparable with those of the most powerful organic-based high explosives currently in use.

The value of harnessing the power of energetic materials has been realized for quite some time, resulting in their pervasive use in diverse commercial processes.[1] Advancements in energetic materials have also been driven by a need to find more powerful, stable, and reliable materials for military devices. Over the past century, the discovery of new, improved energetic materials has lost pace due to the availability of many acceptable materials and their ongoing optimization. Nevertheless, increasing environmental concerns[2] regarding heavy-metal-based primary explosives and rapidly evolving terrorist threats continue to inspire research[3] toward superior energetics.

Beyond commercial considerations, a basic fundamental question in the field of energetic materials remains: How much energy can be stored in an explosive compound while maintaining practical levels of stability? Energetic compounds generate their power by rapid decomposition of chemical bonds to form thermodynamic sinks such as CO_2, H_2O, and N_2. Particularly unstable chemical bonds can be considered "loaded" for rapid decomposition, affording better explosive performance. Yet if the bonds are too unstable, they will not be formed at all, or the formed compound will be too sensitive to handle. Developing energetic materials with high densities provides another route to improved explosive performance without introducing increased instability. The detonation velocity of a material, and thus the intensity of its explosion, is proportional to its density. A notable development in this vein was the synthesis of octanitrocubane[4] (ONC), regarded by many as the most powerful chemical explosive to date. ONC was highly desired because the predicted efficient packing of its cube-like molecules would allow for the highest known density for organic explosives. Another explosive considered in the high-energy community has been hexanitrobenzene (HNB).[5] Remarkably, despite the direct relationship between solid-state structure and explosive performance, single-crystal X-ray studies of some of the most famous energetics have only been undertaken comparatively recently.[6]

Energetic metal salts and complexes offer density beyond the reach of regular organic explosives, and a number of metal-based explosives including lead azide, lead styphnate, and mercury fulminate (MF) have been used as initiation compounds for many decades. However, decomposition of metal–ligand bonds typically affords less energy than that of organic bonds, and metals do not decompose to generate gases like CO_2, N_2, and H_2O, which cause the rapid expansion of an explosion. Hence, these heavy-metal-based explosives have low heats of detonation (ΔH_{det}) per unit mass (kcal/g), and despite high densities, their ΔH_{det} per unit volume (kcal/cm^3) are only slightly higher than that of TNT.

We report here the synthesis, structure determination, and computational analysis of Co- and Ni-based energetic materials in which bridging ligands join adjacent metal centers to form coordination polymers, a class of materials currently being pursued in diverse applications[7] but essentially unexplored in the field of energetic materials. By combining high density, weak precursor bonds, and gas production, these new coordination polymers afford energies of detonation beyond those of all other metal-based explosives to date and on par with the most powerful organic secondary explosives in use today.

To our knowledge, there are no other coordination complex structures with hydrazine as the sole inner-sphere ligand, astounding in view of the numerous and familiar examples of hexamine coordination complexes. Examination of hydrazine-containing coordination compound crystal structures in the Cambridge Structural Database and the Inorganic Crystal

Structure Database reveals that competing ligands or coordinating anions consistently intrude into the inner coordination sphere of the metal, yielding mixed-ligand complexes. There are no reports of crystal structures for metal–hydrazine complexes with non-coordinating anions such as nitrate, perchlorate, tetrafluoroborate, etc. This poses a conspicuous gap in fundamental inorganic structure determination, considering the substantial research activity in the areas of metal–organic frameworks[8] and inorganic cages.[9] The design and preparation of such architectures rely on multidentate ligands and, frequently, non-coordinating anions. The structures reported here provide a starting point for investigating a hitherto overlooked aspect of coordination chemistry.

Our investigation began with a desire to enhance the performance of an initiation compound, nickel hydrazine nitrate (NHN).[10] Although a viable substitute for commonly used metal azides,[11] it possesses relatively low impact sensitivity for this application. Metal perchlorate salts are generally more sensitive than their corresponding nitrates; one attempted preparation of nickel hydrazine perchlorate (NHP) resulted in an explosion.[12] Those authors deemed the substance too sensitive for further investigations, and no reports of this species or its analogues have been made for 60 years. One abbreviated investigation[12] in which no structural information was obtained should not altogether rule out continued efforts to prepare, study, and utilize metal hydrazine perchlorates. It is also important to explore whether substituting the Ni centers with other metals could potentially alter the sensitivity and performance of this class of materials. To this end, we prepared and elucidated the structures of NHP and cobalt hydrazine perchlorate (CHP). Both materials proved to be immensely powerful primary explosives. NHP and CHP crystallize within 1 day following addition of hydrazine to a concentrated aqueous solution of the corresponding metal perchlorate with limited exposure to ambient atmosphere.

As expected, NHP was highly sensitive. Three explosions were observed: first upon grinding, second upon extraction of a 2–3 mg crystal from a vial (the vial was shattered by just this small amount), and third in solution, when an apparently undisturbed vial containing no observable crystalline material exploded without an obvious external stimulus. These observations indicate that NHP has a low critical diameter for detonation. In contrast, CHP could be conveniently initiated by flame, spark, and impact while remaining sufficiently stable for safe handling. CHP responded to a 2.5 kg weight dropped from 20 cm on a drop-hammer apparatus,[13] indicating that it is modestly more sensitive than conventionally used explosives.

Despite obvious difficulties stemming from the high sensitivity (of NHP) and explosive nature of these materials, single-crystal X-ray diffraction (XRD) data were obtained, from which accurate crystal structures were determined. Our analysis indicates that both NHP and CHP crystallize in the monoclinic $P2(1)/n$ space group with two molecules per unit cell and half a molecule per asymmetric unit with very similar unit cell parameters. Both crystals form continuous parallel polymeric chains with every subsequent metal atom bridged to the previous one by a single hydrazine molecule (Figure 1, left). Thus, the octahedral coordination sphere of each metal consists of six hydrazine molecules: four coordinated in a terminal mode, and two employed for bridging with adjacent metal centers. The perchlorates run parallel to the backbones of the coordination polymers with possible H-bonding between
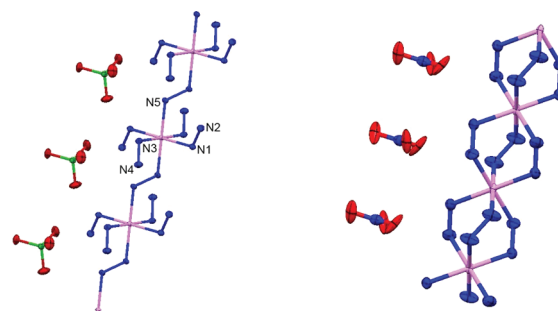

Figure 1. (Left) Crystal structure of NHP. Selected bond distances (Å) and angles (°): Ni–N1, 2.136(1); Ni–N5, 2.117(1); N1–N2, 1.457(1); N1–Ni–N3, 90.84(5); N1–Ni–N5, 92.42(5). (Right) Structure of NHN. Red, O; green, Cl; blue, N; purple, Ni. Ellipsoids are scaled at 50% probability.

perchlorate O's and hydrazine H's, with a closest distance of 2.257 Å. Ni–N bonds range 2.124–2.178 Å, the shortest being associated with the N atom of the bridging hydrazine unit. Co–N bonds are slightly longer, 2.156–2.232 Å, the shortest again being the one with a bridging hydrazine. These are completely in line with average Ni–N and Co–N bonds for coordination compounds. However, the N–N bonds of the bridging hydrazine ligands are elongated to 1.476(2) Å, versus 1.45 ± 0.01 Å for hydrazine monohydrate[14] and 1.46 ± 0.02 Å for hydrazine.[15] Since the position of the H-atoms cannot be accurately determined from XRD, we structurally relaxed the H-atoms by density functional theory (DFT) calculations while keeping the heavy (i.e., non-H) atoms fixed in their XRD-determined positions. The resultant N–H bonds vary between 1.02 and 1.04 Å, in good agreement with an average of 1.015 Å[16] obtained from neutron-diffraction studies on many organic molecules.

The structure of NHN[10] was also elucidated for the first time, albeit with lesser precision than for NHP and CHP. Whereas the perchlorate structures adopt a linear polymeric motif utilizing only one bridging hydrazine, NHN adopts a cage polymer motif in which all hydrazine ligands bridge successive Ni centers (Figure 1, right). Coordination polymer structures have been observed with a single bridging hydrazine in the presence of other co-bridging ligands,[17] as have bis(bridging)[18] hydrazine motifs. NHN represents the first structure of such a tris(bridging) hydrazine cage polymer motif; early spectroscopic evidence suggests such structures are quite general.[19] NHP and CHP are the only structures yet reported in which a single bridging hydrazine defines the backbone of a coordination polymer. Hence, the structures of NHP, CHP, and NHN demonstrate that hydrazine possesses untapped structural potential as a bridging bidentate ligand for construction of inorganic architectures. Non-coordinating anions such as tetrafluoroborate or hexafluorophosphate, which lack the oxidizing nature of nitrate and perchlorate, may yield interesting structures without energetic properties.

The combination of reduced structural reinforcement in the non-bridged polymers, more sensitive perchlorate anion, and higher nitrogen:metal ratio for NHP ($NiN_{10}H_{20}O_8Cl_2$) and CHP ($CoN_{10}H_{20}O_8Cl_2$) is expected to yield increased power and sensitivity compared to NHN ($NiN_8H_{12}O_6$). Additional power for the perchlorate materials could also arise from the likely formation of more stable detonation products, i.e., metal chloride ($NiCl_2$, $CoCl_2$) as opposed to pure metal (Ni) formed by the detonation of NHN.

Given the qualitative observations of the sensitivity and explosive power of NHP and CHP, it was natural to seek theoretical estimates of the heats of explosion for these compounds. First-principles simulations using DFT were used to compute the energies of detonation of the geometry-optimized structures ($\Delta E_{DFT,det}$), defined as the difference between the energies of formation of the explosive and the detonation products. The computed detonation energies were correlated with the known ΔH_{det} for common high explosives (Chart 1). This correlation was then used to estimate the ΔH_{det} of NHN, NHP, and CHP, as displayed in Chart 2, alongside the known values for common energetic materials.

Chart 1. Energy of Detonation for DFT-Optimized Structures ($\Delta E_{DFT,det}$) vs Estimated Heat of Detonation (ΔH_{det}) from Literature for 11 Highly Explosive Materials[a]
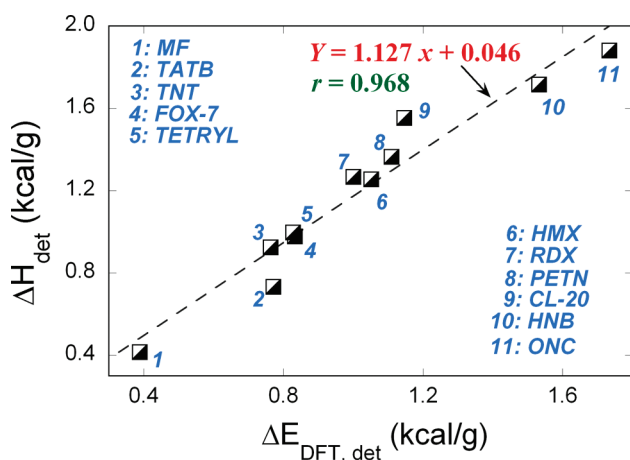
[a] Values are from ref 23 for explosives 1–9 and ref 24 for explosives 10 and 11. MF, mercury fulminate; ONC, octanitrocubane; other abbreviations are common explosive names.

Chart 2. Bar Diagram Representation of the Literature ΔH_{det} Values for the 11 Highly Explosive Materials along with the Predicted ΔH_{det} for NHN, CHP, and NHP Using the Linear Correlation Developed in Chart 1[a]
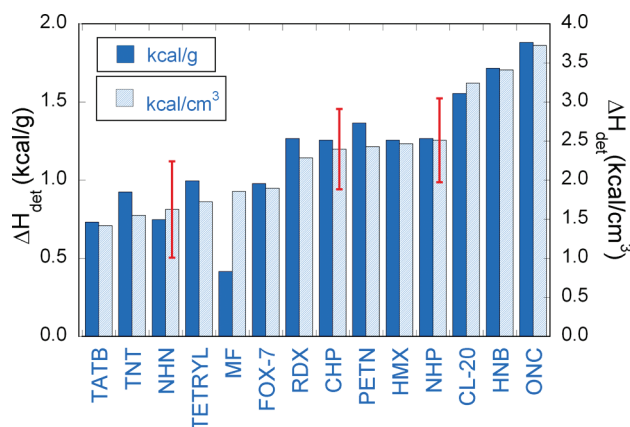
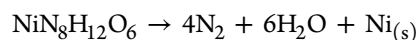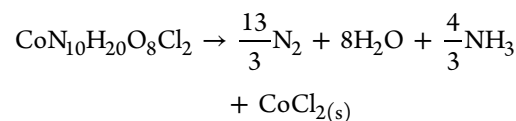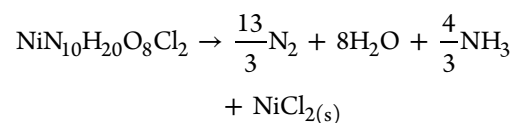[a] Also indicated are the error margins for the predicted values at the 95% confidence level. Both mass-density (kcal/g) and volume-density (kcal/cm^3) of the ΔH_{det} are indicated, and the heats are arranged in increasing order of volume-density.

The extended polymeric backbone structures of NHN, NHP, and CHP prompted the use of all calculations in periodic supercells representing the smallest repeating unit of the explosive. This also accounts for the contribution of the cohesive energy (i.e., heat of sublimation) of the crystalline solid. The DFT code DMol[3,20] was employed, with the electronic wave functions expanded in a double-numeric polarized basis set, while the exchange and correlation effects were incorporated through the gradient-corrected PBE functional.[21] For a periodic calculation, an accurate Brillouin-zone sampling of the reciprocal lattice was also necessary. This was ensured by summation over a finite set of K-points chosen according to the Monkhorst−Pack scheme[22] with a grid spacing of 0.05 Å^{-1}.

For organic (i.e., C, H, N, and O-containing) explosives, the detonation products and their relative abundance were determined by state-of-the-art thermochemical calculations using CHEETAH.[25] For systems with metals, the most stable products were assumed under the constraints of stoichiometrically available oxygen, i.e., $NiCl_2(s)$ for NHP, $CoCl_2(s)$ for CHP, and $Ni(s)$ for NHN. The complete detonation reactions considered for these explosives were

$$NiN_{10}H_{20}O_8Cl_2 \rightarrow \frac{13}{3}N_2 + 8H_2O + \frac{4}{3}NH_3 + NiCl_{2(s)}$$

$$CoN_{10}H_{20}O_8Cl_2 \rightarrow \frac{13}{3}N_2 + 8H_2O + \frac{4}{3}NH_3 + CoCl_{2(s)}$$

$$NiN_8H_{12}O_6 \rightarrow 4N_2 + 6H_2O + Ni_{(s)}$$

All non-metal-containing products, including water, were treated as a gas. Chart 1 plots the computed $\Delta E_{DFT,det}$ values versus the corresponding ΔH_{det} from the literature.[23,24] The data display a strong linear correlation ($r = 0.97$), with the corresponding regression curve indicated by the dashed line. Chart 2 uses this correlation to predict the heats of explosion of CHP, NHP, and NHN and the 95% statistical confidence limits.[26] Two important results are of note: (1) The only published ΔH_{det} value for NHN, 1.014 kcal/g (2.16 kcal/cm^3),[10] is within the error margin but close to the upper limit of our prediction. (2) CHP and NHP appear to possess similar ΔH_{det} (NHP slightly higher), the mean predicted value being similar to those of PETN and RDX, two of the most energetic materials commonly employed. If the actual value is close to the upper 95% confidence limit of our predicted range (as for NHN), ΔH_{det} would be even higher, comparable to that of CL-20. Among metal-containing explosives, NHP and CHP clearly appear to be the strongest known primary explosives, with ΔH_{det} substantially higher than those of MF, lead azide,[23] and NHN.[10]

The synthesis and structural determination of NHP, NHN, and CHP reveal a new class of ionic polymeric energetic materials, comparable with the most powerful explosives in use today. Apart from a traditional detonating role, the low critical diameter indicates that they may be used for microcharges as they can be easily initiated by spark or heat and even quantities of 0.1 mg can release a substantial amount of force. The crystal structures of NHP, NHN, and CHP represent the first examples of coordination complexes with only hydrazine as an inner-sphere ligand and provide the first examples of their respective architectural motifs.

Caution! The materials described here pose extreme explosive hazards, in terms of both sensitivity and explosive power. NHP is sufficiently sensitive to preclude effective characterization beyond the isolation of a single crystal for XRD. The combination of such extreme sensitivity and unpredictability with its tremendous power makes this an exceptionally hazardous material. CHP, though comparatively more stable, is still a sensitive primary explosive and generates extremely high power output. Even small quantities (<1 mg, e.g., a small single crystal) can cause severe physical damage to their surroundings.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and crystallographic statistics; crystallographic CIF files for NHN, NHP, and CHP. This material is available free of charge via the Internet at http://pubs.acs.org.

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