

Perspective

Coordination Energetic Materials—Scientific Curiosity or Future of Energetic Material Applications?

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Abstract: Significant incentives for developing and introducing new energetic materials to the industrial-scale production and application of new energetic materials have stimulated extensive research on the subject. Despite numerous studies, which have reported a broad array of results, progress in this field remains limited as the research results do not translate into commensurate practical applications. Coordination energetic materials are one of the promising classes of such materials. Despite more than two decades of research efforts dedicated to these substances and their advantages over classical energetic materials, in terms of performance parameters and safety parameters, these materials have not found any broader practical application. In this work, selected representative literature reports dedicated to these materials have been analysed in order to present the possible reasons for this state. Some suggestions about the future direction of research and development efforts dedicated to coordination energetic materials have also been formulated. The publication is one voice in the discussion on new challenges related to the search for new lead-free explosives.

Keywords: coordination compounds; energetic materials; application



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1. Introduction

Energetic materials (EMs) are chemical compounds, and their mixtures are capable of rapidly releasing large amounts of energy via chemical chain reactions. These substances are divided into classes (for example, high explosives, low explosives (propellants), and pyrotechnics), based on various criteria, among which the division schemes based on the performance parameters of EM are most relevant in terms of practical applications. From a scientific point of view, however, the division of EMs based on their chemical identity is most relevant. The publication is a concept paper on new challenges related to the search for new lead-free explosives.

Energetic materials can be divided into primary and secondary explosives, based on the differences in their properties. The key feature of primary explosives is that they readily undergo deflagration-to-detonation transition. In the case of lead-based explosives, this process is nigh-instantaneous, making it possible to use relatively small amounts of those compounds as reliable sources of shock waves, used to initiate secondary explosives. Consequently, if these compounds are to be replaced, energetic materials capable of at least comparable facile deflagration-to-detonation transitions should be developed.

Among chemical species classified as energetic materials, coordination energetic materials (CEMs), which are a subspecies of coordination compounds, deserve particular attention. Coordination energetic materials, similar to other coordination compounds, are composed of a central atom (or central atoms in the case of multicore compounds and coordination polymers), organic ligands, and counter-ions. Such materials can exhibit properties intermediate between those of primary and secondary explosives. In contrast to the majority of coordination compounds, the counter-ions present in CEM molecules

are typically oxidising in nature, e.g., NO_3^- , ClO_4^- . Simultaneously, the organic ligands present in CEMs are frequently rich in nitrogen atoms, as tends to be the case with many classical EMs.

Literature reports indicate that high nitrogen content in ligands is desirable because a large amount of energy is stored in their structure. Therefore, during the decomposition reaction of the product, the number of gaseous products from the decomposition increases (increasing the ratio of gaseous nitrogen to carbon dioxide). This has the advantage of reducing the release of harmful carbon monoxide into the atmosphere. An increase in the nitrogen content of the molecule is associated with an increase in the heat of formation and an increase in the density of the material. These parameters, in turn, are related to the parameters of the detonation process, affecting, for example, the increase in detonation velocity of coordination explosives [1,2].

Literature sources have reported the successful synthesis of a staggering number of CEMs and have detailed the properties of CEMs with an extreme variety of chemical structures. Coordination energetic materials are typically presented as “green” energetic materials that fulfil the requirements of sustainable development and can be an alternative to lead-containing EMs, such as lead(II) azide or lead(II) styphnate. Lead(II) azide is one of the most widely used classical EMs. Its advantages include rapid deflagration to detonation transition; reliability; and a straightforward and low-cost synthesis procedure. On the other hand, it also has multiple drawbacks as at ambient conditions it slowly undergoes decomposition, releasing hydrazoic acid, and both it and the raw materials for its production are extremely toxic and harmful to the environment.

Despite the severe drawbacks of lead(II) azide and the advantages of CEMs reported in literature over the last two decades, even until now lead(II) azide has not been replaced in its typical applications. The aim of this work is to discuss the possible reasons for this state and to indicate a direction for the further development of coordination energetic materials that will potentially be more useful in terms of practical applications.

2. CEMs—State of the Art

2.1. Synthesis of Coordination Energetic Materials

Coordination energetic materials are prepared via the complexing reaction, carried out between a transition metal compound and a ligand—an organic nitrogen compound, which typically contains amine groups (Figure 1). This reaction is supposed to be straightforward and quantitative in nature, requiring only that the reaction medium is a solvent for the employed raw materials. According to literature reports, after a CEM is prepared, it is possible to modify its chemical structure by exchanging the counter-ion present in the CEM molecule or by producing salts, through the reaction of the CEM with acids [3].

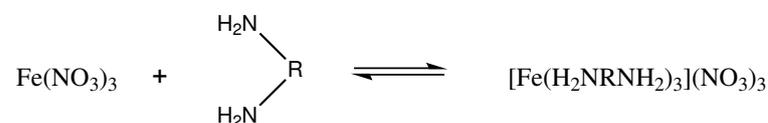


Figure 1. CEM synthesis reaction example using iron(III) nitrate(V) and an alkylenediamine.

In regard to the choice of counter-ion, it was found that CEMs bearing azides as counter-ions typically show increased sensitivity to mechanical stimuli. In turn, using counter-ions rich in active oxygen, such as nitrates or perchlorates, helps improve the oxygen balance of the CEM, increasing the amount of energy released during the decomposition of the CEMs [4].

2.2. Nitrogen-Rich Organic Ligands

According to literature reports, the ligands most typically used to produce coordination energetic materials are hydrazine, aliphatic amines, heterocyclic compounds, and mixed-functionality compounds, such as heterocyclic compounds functionalized with amine groups (Table 1). Many authors [4] indicate the dependence of performance param-

ters of CEMs on the content of nitrogen atoms in the ligands composing the CEMs. It should be noted, however, that such structure–property relationships are typically established within a narrow subgroup of ligands that are similar in terms of their chemical structure.

From the perspective of coordination energetic materials, high nitrogen content in the ligand molecule is desirable, due to the increased nitrogen/carbon dioxide ratio in the decomposition products of CEMs. High nitrogen content also reduces the emission of the toxic carbon monoxide in the case of CEMs, whose decomposition requires the consumption of significant amounts of oxygen from air (Figure 2). High nitrogen content is also associated with increased density [5] and heat of formation of the CEM. Increasing these two parameters has a direct, positive effect on the parameters of detonation of the CEM [6].

Ethylenediamine is a frequently used bidentate ligand that contains 46.61 wt. % nitrogen. CEMs containing ethylenediamine ligands typically show good thermal stability and average sensitivity to mechanical stimuli [7]. Hydrazine is another commonly used bidentate ligand, containing a remarkable 87.42 wt. % nitrogen. CEMs containing hydrazine ligands typically show an affinity to decompose via detonation and exhibit mechanical sensitivity comparable to that of initiating EMs [8,9].

Among other works utilizing ligands that are aliphatic compounds, it is worth mentioning the use of oxidized triaminoguanidines, which contain 83.97 wt. % nitrogen. Literature reports state that CEMs containing such ligands are practically insensitive to mechanical stimuli, exhibit high thermal stability and high density, and are predicted to have detonation velocities in the order of 5–9 km/s [10].

Heterocyclic compounds, such as triazoles, tetrazole, and their derivatives, are another group of organic ligands. Such ligands contain from approx. 40 up to even 80 wt. % nitrogen and exhibit a great variety of properties [11]. CEMs containing fulminate anions are interesting examples of compounds containing such heterocyclic ligands [12].

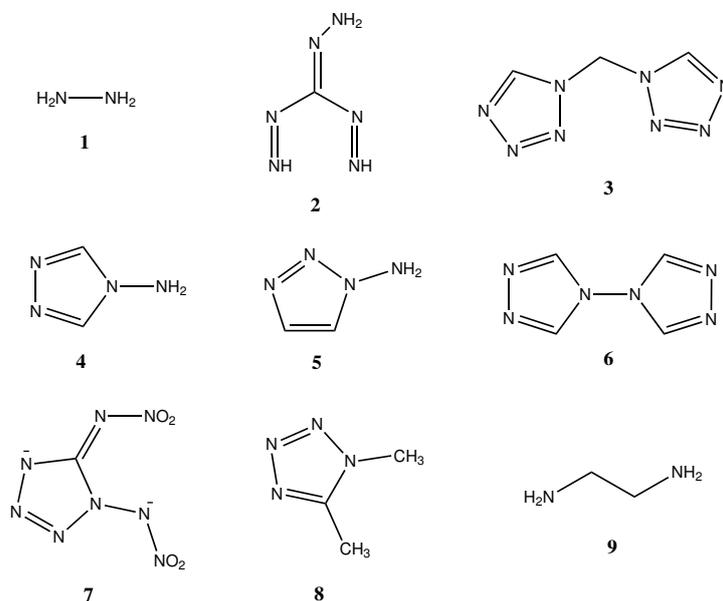


Figure 2. Structure of selected organic ligands reported to be used to produce CEMs.

Table 1. Selected organic ligands reported to be used to produce CEMs, sorted by their nitrogen atom content (by weight).

Chemical Structure	Nitrogen Content [wt. %]	Name Abbreviation	Ref.
1	87.42	Hz	[7]
2	83.97	OxTANQ	[10]
3	73.66	bisTetrAzM	[12]
4	66.64	4A124TrAz	[12]

Table 1. Cont.

Chemical Structure	Nitrogen Content [wt. %]	Name Abbreviation	Ref.
5	66.64	1A123TrAz	[11]
6	61.74	bisTrAz	[12]
7	59.58	DNAT	[13]
8	57.11	DMTetrAz	[12]
9	46.61	EDA	[8,9]

2.3. Transition Metal Compounds

The successful preparation of coordination energetic materials relies on the use of transition metal compounds. Despite there existing reports of CEMs containing heavy metals, the majority of reports focus on transition metals belonging to the fourth period of the periodic table of elements [14,15]. Those elements form relatively small ions with a high charge and typically exhibit little to no toxicity and environmental impact. In some cases, the desired compounds are found in the environment as minerals. Among the CEMs reported in the literature, the most frequent mentions are made of compounds in which the role of the central atom is fulfilled by cations such as Cr^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} [16–18]. Period 4 metal compounds are characterized by high spatial packing. These metals are characterized by an unfilled d-substrate, so they can exist on many different oxidation levels. The coordination number of the abovementioned cations is 6, except for the copper cation, whose coordination number is 4. Site coordination in the case of multidentate ligands provides the possibility of coordinating larger numbers of ligand molecules relative to metal salt molecules; the structures of these compounds are mostly octahedral and, except for mercury and copper, are characterized by a flat-coordinated geometry [16]. Compounds based on some of these elements, such as copper and cobalt, are not necessarily completely “green” as some forms of those elements show toxicity, but despite this, they are far more desirable than compounds based on lead.

2.4. Performance Parameters of Coordination Energetic Materials

The performance parameters of CEMs reported in the literature are extremely varied, and the materials are only able to undergo decomposition via deflagration to substances, whose parameters are comparable to those of the strongest classical EMs [10]. A similar variation can be observed in terms of the safety parameters of the reported CEMs as some of the reported substances show sensitivity comparable to that of lead(II) azide, whereas other compounds are virtually insensitive to mechanical stimuli. The majority of works dedicated to CEMs, however, report substances whose performance parameters are comparable to those of 1,3,5-trinitro-1,3,5-triazinane (“hexogen”, RDX) and that are slightly more sensitive to stimuli than RDX. The performance and safety parameters of selected CEMs and classical EMs containing lead are collated in Table 2.

Table 2. Sensitivity and performance parameters of selected CEMs compared with classical EMs.

Compound	Sensitivity Parameters		Performance Parameters		Ref.
	Friction [N]	Impact [J]	Detonation Velocity [m/s]	Detonation Pressure [GPa]	
Lead(II) azide	0.1–1.0	2.5–4.0	5877	33.4	[19,20]
	0.196 ^a	0.41 ^b	4630	16.1	[8]
Lead(II) styphnate	0.5–1.5	2.5–5.0	-	-	[21]
[Ni(Hz) ₃](NO ₃)	15.69 ^a	0.82 ^b	7000	20.8	[8]
[Ag(4 A124 TrAz) ₃ (H ₂ O)]ClO ₄	30	2	-	-	[22]
[Ag ₄ (CNO) ₄ (bisTrAz)]	10	5	-	-	[12]
[Ag ₃ (CNO) ₃ (bisTetrAzM) ₃]	64	7	-	-	[12]
[Cu(OxTANQ)]Cl	>360	>98	8969	13.5	[10]
[FeK ₂ (DNAT) ₂ (H ₂ O) ₄]	3	16	8147	29.8	[13]
[CuK ₂ (DNAT) ₂ (H ₂ O) ₄]	3	16	8348	31.5	[13]
[NiK ₂ (DNAT) ₂ (H ₂ O) ₄]	6	26	8169	29.7	[13]

Table 2. Cont.

$[\text{CoK}_2(\text{DNAT})_2(\text{H}_2\text{O})_4]$	5	22	8187	30.3	[13]
$[\text{ZnK}_2(\text{DNAT})_2(\text{H}_2\text{O})_4]$	4	18	8478	32.8	[13]

^a Recalculated from imperial units. ^b Recalculated based on experimental data, energy corresponding to 50% initiation chance.

3. Discussion

3.1. Criteria for Application of New Energetic Materials

In order for a new energetic material to find any military or civilian application, it must exhibit the desired performance parameters (e.g., an ability to perform mechanical work) and safety parameters (e.g., sensitivity to mechanical stimuli). Fulfilling these criteria may, in some cases, be sufficient for a new EM to find application, but in the vast majority of applications, a new EM must compete with existing material solutions. The issue of new EMs showing better performance than existing solutions is further complicated by the requirements imposed by national, foreign, and international law, requiring any EMs introduced to the market to fulfil additional criteria. These additional criteria currently focus on meeting the assumptions of sustainable development [20] and minimizing the harmful effects of the EM on humans and on the environment. It should be noted that the “Green Deal” policy adopted by the European Union is aimed, among others, at replacing environmentally harmful materials with alternative materials that meet the requirements of “green chemistry”. Taking into consideration the recent ban on the use of lead ammo in wetlands, due to its environmental effect [23], it is not impossible for the support for “green” solutions to be replaced in the future by a demand to cease using the most toxic and environmentally harmful substances. The elimination of harmful substances from use may not be limited only to the properties of the end products, as, according to the ideas of “green chemistry” the entire manufacturing process should be considered. Even if the end product shows little toxicity or environmental impact, it may need to be eliminated from use if the use of harmful substances is required for its production. In the case of the energetic materials industry, the most glaring examples of harmful substances are EMs containing lead. Among lead-containing EMs, lead(II) azide is a particular issue in this regard as its toxicity stems from both the lead cation and from the azide anion. Simultaneously, the issue of its insufficient safety parameters is an issue that has been raised for many years. Why, therefore, in light of numerous CEMs that exhibit similar energetic properties and more favorable safety properties (Table 2), was this compound not retired from production?

The basic susceptibility parameters of classical explosives, depending on their type, are characterized by different values of performance parameters. Similar variability may be observed as far as safety parameters are concerned, where some of the substances described in the literature are characterized by sensitivity parameters comparable to those of lead azide(II) and some are practically insensitive to mechanical stimuli. It can be noted that most of the compounds described in the literature are similar in terms of sensitivity parameters to mechanical stimuli to 1,3,5-trinitro-1,3,5-triazacyclohexane, also commercially available under the name hexogen, or show slightly higher sensitivity values. The table (Table 2) shows the sensitivity values for the selected compounds compared to the sensitivity values for the currently used initiating explosives. The table shows that most of the present compounds e.g., containing 1,5-di(nitramino)tetrazolium (DNAT), have relatively low friction sensitivity while maintaining high detonation velocity. From the point of view of performance and consequently application, the use of the mentioned compound is associated with a high risk of detonation when working with the mentioned material. Nowadays, it would be a great advantage to find new compounds that would be safer in use, which is one of the aims of this project.

3.2. Practical Considerations

The coordination energetic materials described above, despite multiple advantages over lead(II) azide, have until now failed to find broader applications. This stems from

the fact that among the ligands composing those compounds **1**, only a few substances are produced on an industrial scale. Aliphatic diamines, such as ethylenediamine and its homologues, whose global annual production is on the order of hundreds of thousands of tons (demand in 2012 is reported as 400,000 t) [24], can be an example of such substances. Considering the industrial production of high-energy materials, most of the ligands that constitute the basic building unit of CEMs, despite exhibiting favorable energetic properties, are produced by multi-step organic synthesis. Consequently, the final unit price of these compounds is high and their availability is significantly limited. Despite favorable properties and competitiveness of many CEMs mentioned above, their practical application would require extreme investment costs, associated with the need to begin the production of the required ligands. Depending on the selected ligand, the process of producing CEMs from chemical raw materials available on an industrial scale may be composed of five to even twenty fundamental chemical reaction steps, each requiring relevant precipitation and purification steps.

4. Summary

To summarize, even though coordination energetic materials can be a competitive alternative to classical EMs, it may be justified to adjust the direction of research and development efforts dedicated to CEMs. Focusing research efforts on CEMs, whose ligands are either typical raw materials of the chemical industry or can be prepared from such raw materials through straightforward processes, appears to be favorable. Aliphatic diamines can be an example of such ligands as they have a relatively high nitrogen atom content, lead to CEMs with a broad range of properties, and exhibit relatively limited toxicity and environmental impact.

The choice of central atoms forming the CEMs is generally less problematic. The salts of metals capable of producing coordination compounds are common raw materials of the chemical industry and, in many cases, their use is not associated with any significant environmental impact. Therefore, despite the limitation in the feasibility of using some organic ligands, there exists a broad range of CEMs, which can find practical application and in the future finally replace some classical EMs, such as lead(II) azide.

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Abbreviations

EM	energetic material
CEM	coordination energetic materials
Hz	hydrazine
OxTANQ	oxidized triaminoguanidine
bisTetrAzM	bis(2-tetrazolyl)methane
4A124TrAz	4-amino-1,2,4-triazole
1A123TrAz	1-amino-1,2,3-triazole
bisTrAz	4,4'-bi-1,2,4-triazole
DNAT	1,5-di(nitramino)tetrazole

DMTetrAz	1,5-dimethyltetrazole
EDA	1,2-ethylenediamine

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