APPLICATION OF HIGH-ENERGY COORDINATION COMPOUND AS NEW "GREEN" ENERGETIC MATERIALS

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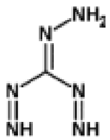
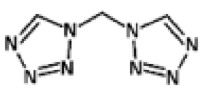
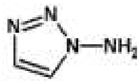
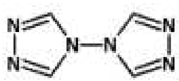
Despite the important factors promoting the development, implementation into industrial scale production and application of new high-energy materials, the progress in this field is limited, due to safety at work and environmental aspect. Nevertheless, there is a group of compounds that can potentially exhibit high-energy properties, being coordination compounds, while not being harmful to the environment. Despite more than two decades of work on these substances and their advantage over classical high-energy materials resulting from more favorable performance and safety parameters, these materials have not found broader practical application.

Coordination energetic materials (CEMs), like other coordination compounds, consist of a central atom (or central atoms in the case of multicore compounds and also the so-called coordination polymers), organic ligands, and counter-ions (anions of acidic residues). By changing one of the building blocks, new compounds with different physicochemical and energetic properties can be obtained. One of the groups that are still being studied are compounds derived from transition metal nitrates(V) and chlorates(VII) due to their high availability and non-toxicity. Unlike most coordination compounds, the counter-ions that build the KMW molecules are most often in the nature of oxidants, e.g. NO_3^-, ClO_4^-. Oxidizing anions provide a complementary ion for complex cations and allow the release of large amounts of active oxygen. At the same time, organic ligands present in CEMs molecules should be characterized by a high content of nitrogen atoms, as is the case for many classical energetic materials (EMs). In addition, the selection of appropriate organic ligands with high nitrogen content enables the synthesis of coordination compounds having similar energetic parameters with regard to lead azide.

When selecting the ligands necessary for the fabrication of CEMs, attention should be given to the nitrogen content of the molecule. Many authors mention the dependence of nitrogen content on the performance of materials, but for a small group of compounds [1]. From the point of view of "green chemistry", high nitrogen content is favorable because it allows increasing the ratio of gaseous nitrogen to carbon dioxide in decomposition products. In addition, as the density [2] and heat of formation of CEMs increases, the performance of the detonation process is improved [3]. Literature reports on the use of high-energy organic ligands indicate the use of hydrazine, aliphatic amines, heterocyclic compounds or compounds with mixed functionality, as shown in the following table (Table 1).

One of the commonly used ligands with high nitrogen content is hydrazine, which contains 87.42% nitrogen atoms in the molecule. CEMs containing hydrazine in their structure, exhibit a high tendency to decompose by detonation and have comparable sensitivity to mechanical stimuli to that of initiating explosives [8]. Ligands containing triaminoguanidine derivatives with a nitrogen content of 83.97% are also noteworthy, due to their low sensitivity to mechanical stimuli, high density, good thermal stability, and detonation velocity ranging from 5 to 9 km/s [5].

Table 1 Selected organic ligands used to produce CEMs, ordered by weight nitrogen content (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).

Chemical structure	**Nitrogen content [%]**	**Name abbreviation**	**Ref.**
	87,42	Hz	[4]
	83,97	OxTANQ	[5]
	73,66	bisTetrAzM	[6]
	66,64	4A124TrAz	[6]
	66,64	1A123TrAz	[7]
	61,74	bisTrAz	[6]

The synthesis of high-energy complexes compounds is associated with the use of transition metal compounds belonging to the fourth period of the periodic table of elements. These elements form small ions with high charge and are mostly characterized by low toxicity and environmental harmfulness. In many cases, desirable compounds of these metals occur in nature as minerals. Moreover, their characteristic feature is an unfilled d-sublayer, allowing them to occur at different oxidation levels. Among the CEMs reported in the literature, the most frequently mentioned compounds are those in which cations such as Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} , act as the central atom. The coordination number of these cations is 6, except for the copper cation, which has a coordination number of 4. Compounds of some of these elements, e.g., copper and cobalt, cannot be considered fully "green" because they may exhibit some toxicity, but they are nonetheless much more desirable than lead compounds.

Literature sources report the successful receipt and properties of a vast number of CEMs. These substances are often referred to as "green" EMs, which meet sustainability requirements and which can provide alternatives to lead-containing EMs such as lead(II) azide, or lead styphnate. Lead(II) azide is one of the most widely used classical EMs. Its advantages include rapid transition from deflagration to detonation, reliability, and simple synthesis at low cost. On the other hand, it has many drawbacks, as it decomposes under ambient conditions with the release of hydrazolic acid, and both it and the substrates for its production are characterized by extremely high toxicity and environmental harm. In spite of the significant drawbacks of lead azide(II), to this day lead azide(II) has not been displaced from its current applications.

Coordination energetic materials are obtained by a quantitative complexation reaction between a transition metal compound and an organic ligand, typically of aliphatic or aromatic amine nature (Figure 1). An additional advantage of CEMs syntheses is the use of such a reaction medium, which will constitute a solvent for the substrates used for instance water. It is worth noting that these compounds can be modified by replacing the counterion that is part of the CEMs molecule [11] , or by obtaining their salts by reaction with acids [12].

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

Production and use of many high-energy materials is associated with release into the environment (soil, surface and ground water, atmosphere) of substances that adversely affect humans and the environment. Environmental harm and significant toxicity have been among the main reasons for the withdrawal of many high-energy materials (e.g. mercury salts) from industrial use. On the other hand, efforts to discontinue the industrial use of high-energy materials with significant environmental harm or toxicity have been effective only to a limited extent. Therefore, the important thing is to strive for materials that do not pose a threat to the environment.

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