ENERGETIC COORDINATION COMPOUNDS AS POTENTIAL ALTERNATIVES TO CURRENTLY USED LEAD-CONTAINING COMPOUNDS

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Energetic coordination compounds (ECCs) are one of the most intensively investigated groups of energetic materials (EMs). Coordination compounds can possess properties that are intermediary between primary and secondary explosives. Simultaneously ECCs, depending on their structure, exhibit none or only negligible harmfulness towards humans and the environment. These compounds, like other coordination compounds, consist of a central atom (or central atoms in the case of multicore compounds), organic ligands and counter-ions.

The aforementioned compounds are described in literature as potential alternatives to primary explosives that are lead compounds, such as lead (II) azide and lead (II) 2,4,6-trinitroresorcinate. Many ECCs containing copper as a central atom are reported in literature. Despite the ability of such compounds to exhibit high detonation characteristics (e.g., high detonation velocity), they tend to present high sensitivity to mechanical stimuli, which precludes any application due to safety issues. For instance, the compound $[Cu_2(N_3)_4(BTRI)]$ (BTRI = 4,4'-bis(1,2,4-triazole)), has been reported to exhibit a sensitivity to impact of 2 J, a sensitivity to friction of ≤ 0.1 N and sensitivity to electrostatic discharge of 5 mJ, while the velocity of detonation is 8.28 km/s. [1]. Therefore, it is reasonable to find new ECCs with specific properties, while maintaining the safety of working with these materials.

According to literature reports, ECCs should contain nitrogen-rich ligands and central atoms that are either non-toxic or exhibit only minimal toxicity. These central atoms are typically d-block metal cations [2]. Unlike most coordination compounds, counter-ions that typically exhibit an oxidative nature are present in the molecules of ECCs, such as NO_3^-, ClO_4^-. [3].

Based on literature reports, compounds belonging to the group of heterocyclic compounds are often investigated due to their high stability or high heat of formation [4]. Nitrogen present in the molecule of heterocyclic compounds mostly occurs on negative oxidation degrees, consequently, as results of their decomposition, environmentally non-toxic N_2 is emitted [5].

Triazoles, tetrazoles and their derivatives are widely as ligands in the synthesis of ECCs. These compounds contain from about 40% to 80% by weight of nitrogen and have diversified properties including sensitivity to mechanical stimuli [6]. One example is compounds containing 1H,4′H-[3,3′-bis(1,2,4-triazole)]-4′,5,5′-triamine ($C_4H_7N_9$) with a nitrogen content of 69.6 wt %. They exhibit an alkaline-acid characteristic due to their ability to accept two protons or lose one proton [7]. Considering heterocyclic compounds, many coordination compounds based on 4-aminotriazole can be found in the literature functioning as a ligand, such as 1-amino-1,2,4-triazole and 1-amino-1,2,3-triazole (1- ATRI). The use of N1-substituted aminotriazoles increases the energy content of coordination compounds. The following table presents selected properties of coordination compounds containing 1-ATRI (Table 1).

Table 1 Properties of selected energetic coordination compounds, where a - decomposition temperature; b - sensitivity to impact; c - sensitivity to friction; c - sensitivity to electrostatic discharge [8]

Związek	**$T_{dec.}$ [°C]^a**	**IS [J]^b**	**FS [N]^c**	**ESD [J]^d**
$[Cu(NO_3)_2(\mu-1-ATRI)_2]$	167	<1	30	0.10
$[Cu(H_2O)_4(1-ATRI)_2](PA)_2$	188	>40	>360	1.22
$[Cu(HTNR)_2(1-ATRI)_2]$	177	1.5	80	0.04
$[Cu(H_2O)_2(1-ATRI)_4](H_2TNPG)_2$	153	2	160	0.30
$[Cu(\mu-TNR)(1-ATRI)_2]$	194	3	60	0.05
$[Cu(H_2O)_2(1-ATRI)_4](ClO_4)_2$	167	1	0.45	0.10
$[Fe(1-ATRI)_6](ClO_4)_2$	166	1.5	2	0.04
$[Zn(1-ATRI)_6](ClO_4)_2$	188	3	6.75	0.07
$[Zn(1-ATRI)_4](NO_3)_2$	188	6	45	0.70
$[Cu(\mu-TNR)(1-A-1,2,4-TRI)_2]$	132	<1	23	0.01

Considering aliphatic compounds, one example of a commonly used ligand is ethylenediamine, which is a bidentate ligand. This compound contains 46.61 wt % nitrogen and the coordination compounds incorporating this ligand are characterized by high thermal stability and average sensitivity to simple stimuli [9]. Another bicyclic ligand is hydrazine, containing 87.42 % nitrogen by weight. Unlike ethylenediamine, the literature indicates that hydrazine-containing compounds have properties similar to initiating explosives [10]. Furthermore, among the current research work, we can find some information on the use of aminoguanidine derivatives, containing 83.97 % nitrogen by weight. This ligand, used in the synthesis of EMs, provides high thermal stability of the obtained compound and has high density with negligible sensitivity to simple stimuli [11].

An example of coordination compounds containing a ligand in the form of hydrazine is nickel(II) hydrazine nitrate $Ni(N_2H_4)_3(NO_3)_2$ or a perchlorate analog. Taking into account the calculated detonation velocity of VOD > 8000 m/s, as well as high sensitivity to mechanical stimuli, the nitrate analogue is currently used [12]. The article [13] reports that its detonation velocity is 7000 m/s, friction sensitivity is 10 N, impact 80 J, electrostatic discharge sensitivity 0.001 J and ignition temperature is 219 °C, which makes it a safer material to handle.

There are also coordination compounds containing ligands with oxygen chain form, such as carbohydrazide (CHZ) [14]. Examples include ECCs containing metal carbohydrazide perchlorates $M(CHZ)_3(ClO_4)_2$ (M=Mn, Fe, Co, Ni, Cu, Zn), for which compounds with Zn are the most stable and environmentally friendly, while the breakdown of the Zn-N bond initiates decomposition of the material [15]. In addition, Zn^{2+} in coordination compounds (ZnCP) is used as both a catalyst and anion carrier during the decomposition process (continuous decomposition in the temperature range of 280 - 340 °C). The ability to coordinate Zn with the three CHZ ligands is possible via an oxygen atom, as well as terminal nitrogen atoms [16].

Energetic coordination compounds may offer alternatives as new green explosive initiators. These compounds can contain ligands in the nature of aliphatic amines, or heterocyclic compounds. The possibility of modifying the molecule in the various stages of synthesis, gives the possibility of obtaining a variety of compounds. Some of them have low toxicity, making them a substitute for lead azide, which is used in industry. Modern explosives should be characterized by the best possible detonation parameters, while ensuring the greatest possible safety in working.

References

1 Wurzenberger, M. H., Gruhne, M. S., Lommel, M., Szimhardt, N., & Stierstorfer, J. (2022). Advancement and stabilization of copper (ii) azide by the use of triazole-and tetrazole ligands–enhanced primary explosives. Materials Advances, 3(1), 579-591

2 Xu, J. G., Li, X. Z., Wu, H. F., Zheng, F. K., Chen, J., & Guo, G. C. (2019). Substitution of nitrogen-rich linkers with insensitive linkers in azide-based energetic coordination polymers toward safe energetic materials. Crystal Growth & Design, 19(7), 3934-3944

3 Kofen, M., Harter, A. G., Klapötke, T. M., & Stierstorfer, J. (2022). 1, 5-Dimethyltetrazole as a ligand in energetic 3d5 to 3d10-metal coordination compounds. *Energetic Materials Frontiers*, *3*(3), 111-121

4 Keshavarz, M. H., & Klapötke, T. M. (2021). The properties of energetic materials. In The Properties of Energetic Materials. de Gruyter

5 Parisi, E., Landi, A., Fusco, S., Manfredi, C., Peluso, A., Wahler, S., ... & Centore, R. (2021). High-energy-density materials: an amphoteric N-rich bis (triazole) and salts of its cationic and anionic species. *Inorganic chemistry*, *60*(21), 16213-16222

6 Szimhardt, N., Wurzenberger, M. H., Zeisel, L., Gruhne, M. S., Lommel, M., Klapötke, T. M., Stierstorfer J., 1-AminoTriazole Transition-Metal Complexes as Laser-Ignitable and Le-ad-Free Primary Explosives, Chemistry–A European Journal, 25, 8, 1963-1974, 2019

7 Parisi, E., Landi, A., Fusco, S., Manfredi, C., Peluso, A., Wahler, S., ... & Centore, R. (2021). High-energy-density materials: an amphoteric N-rich bis (triazole) and salts of its cationic and anionic species. *Inorganic chemistry*, *60*(21), 16213-16222

8 Yan Q. L., Cohen A., Petrutik N., Shlomovich A., Zhang J. G., Gozin M, Formation of highly thermostable copper-containing energetic coordination polymers based on oxidized triaminoguanidine. ACS applied materials & interfaces, 8, 33, 21674-21682, 2016

9 Bi-Dong W., Zun-Ning Z., Fu-Gang L., Yang L., Tong-Lai Z., Jian-Guo Z., Preparation, cry-stal structures, thermal decompositions and explosive properties of two new high-nitrogen azide ethylenediamine energetic compounds, New Journal of Chemistry, 37(3):646–653, 2013

10 Hariharanth B., Chandrabhanu K. S., Rajendran A. G., Ravindran M., Kartha C. B., Detona-tor using nickel hydrazine nitrate as primary explosive, Defence Science Journal, 56, 3, p. 383, 2006

11 Yan Q. L., Cohen A., Petrutik N., Shlomovich A., Zhang J. G., Gozin M, Formation of highly thermostable copper-containing energetic coordination polymers based on oxidized triaminoguanidine. ACS applied materials & interfaces, 8, 33, 21674-21682, 2016

12 Cartwright, M. Investigation of preparation, solubility and stability properties of nickel hydrazine nitrate (NiHN). Propellants, 979. Explosives, Pyrotechnics 2018, 43, 1270–1276

13 Chhabra, J.; Talawar, M.; Makashir, P.; Asthana, S.; Singh, H. Synthesis, characterization and thermal studies of (Ni/Co) metal 981 salts of hydrazine: potential initiatory compounds. Journal of hazardous materials 2003, 99, 225–239

14 Zhang, J.; Zhang, T.; Zhang, J.; Yang, L.; Cui, Y.; Hu, X.; Liu, Z. Synthesis, crystal structure and thermal decomposition character 695 of $[Zn(CHZ)_3][C(NO_2)_3]_2(H_2O)_2$ (CHZ=Carbohydrazide). Structural Chemistry 2008, 19, 321–328

15 Joas, M.; Klapötke, T.M. Laser Initiation of Tris (carbohydrazide) metal (II) Perchlorates and Bis (carbohydrazide) diperchlorato- 830 copper (II). Propellants, Explosives, Pyrotechnics 2015, 40, 246–252

16 Wang, K.; Dai, C.; Sun, C.; Cheng, L.; Zhang, J.; Zhang, T. The effects of Zn2+ and ClO_4^- in the excellent primary explosive Zn 828 $(CHZ)_3(ClO_4)_2$. International Journal of Quantum Chemistry 2020, 120, e26107