



Coordination compounds as potential explosives

Surabhi Sinha*

Department of Chemistry, United College of Engineering & Research Naini, Prayagraj, 211010 India,

ARTICLE INFO

Article history:

Received 25 November 2018

Received in revised form 7 December 2018

Accepted 19 December 2018

Available online 21 December 2018

Keywords:

Oxidizers

Perchlorate complexes

Explosive

coordination compounds

ABSTRACT

Explosive coordination compounds are topic of distinct interest owing to specific application of some of them particularly as safe primary explosives or igniters. Explosive properties of coordination compounds tested varied over a wide range depend on several factors. Present article focuses on general principles of designing explosive coordination compounds and in the light of experimental findings a plausible combustion mechanism of coordination compounds has been suggested.

1. Introduction

Earlier explosives were recognized to be only nitro compounds or alcohol nitrates. Compounds such as azides or fulminates which were able to explode, and were used as primary explosives in detonation or ignition caps were also considered as explosives. Potential applicability of transition metal compounds as explosives especially as primary explosive was first reported in late fifties and early sixties of the previous century. With the development of explosives like NHN [tris(hydrazine)nickel(II) nitrate(V)] and HATP [di(3-hydrazino-4-amino-1,2,3-triazole)copper(II) perchlorate]^[1-3] a renewed interest was observed in the eighties in this area. Initiation of explosives requires primaries which are chemical compound or mixtures. These are used in igniters and detonators. Almost endless possibilities exist for combining metal atoms, ligands and ions. Explosive coordination compounds are considered as safe primary explosives or igniters^[4,5] making it subject of considerable interest. The burning rate of an explosive compound depends largely on two factors: nature of oxidizers and nature of central metal ion.

2. Design

Capability of a substances to create explosion lies in the chemical structure of coordination compounds with common chemical formula: $[ML_n](OX)_m$, where M is central metal atom, L is ammonia or organic based ligand and OX is anion. Compositions in which metal atom, fuel and oxidizers are mixed at molecular level are considered as energetic composition.

3. Metal

Explosive coordination compounds should have unvarying

composition and be stable under ambient condition in solid state. This requirement is mainly ensured by nature of central metal atom^[6]. Stable compounds are mainly of metals of Group I and Group II viz. Cu, Ag, Zn and Cd. Because of well known catalytic properties Pb is of prime importance among heavy metals. Pb salts with nitrophenols possess initiating ability^[7]. Salts of bivalent metals form stable complex with various organic compounds. For transition metals showing strong oxidizing it is not possible to obtain coordination compounds owing to redox reaction between metal and ligand.

Alkali metals have little tendency to complex formation, nitrogen containing ligands which are most interesting from the point of view of making explosive coordination compounds, are usually sensitive to moisture. The perchlorate complexes with hydrazine are known only for Li and Na having strong tendency of complex formation among alkali metals.^[8] In comparison to alkali metals alkaline earth metals show noticeably larger tendency to complex formation, except for the metal ions possessing small size because of their tendency to form stable hydroxo and oxo-complexes of non explosive nature.

Sum of oxidizing group defines valence of central metal whereas the coordination number of metal controls the fuel contents in the molecule. Thus, fuel oxidizer ratio is regulated by changes in the valence of metal atom and its coordination number. A number of metals, such as Cu, Ni, Zn and Cd permit synthesis of coordination compounds with various numbers of ligands in the molecule. Such as, 4-amino-1,2,4-triazole is able to coordinate to both copper perchlorate and nitrate to form coordination compound with two (CN=4) or three (CN=6) ligands. The fuel-oxidizer ratio exerts a major effect on energetic characteristics of explosive compounds.

* Corresponding author. e-mail: rush2surabhi@yahoo.com

4. Oxidizer

Anions in the complexes under consideration act as oxidizers. The coordination compounds should contain such molecular fragments which possess oxidizing properties either themselves or on destruction, these are usually ClO_4^- and NO_3^- and similar counter ions such as ClO_3^- , NO_2^- , IO_3^- , IO_4^- , BrO_3^- , MnO_4^- as well as various nitro- containing compounds such as $\text{C}(\text{NO}_2)_3^-$, $\text{N}(\text{NO}_2)_2^-$ and Picrate (Pic). Nature of anion has major effect on the physiochemical and explosive properties of coordination complexes such as thermal stability, solubility, flash point and impact sensitivity^[9]. Choice of anion and physiological properties of coordination compounds with the chosen anion considerably affects the heat of explosion. Very often chemical nature of anion affects number of ligands in the coordination compounds. Anion such as NO_2^- , IO_3^- , IO_4^- , BrO_3^- , MnO_4^- exhibit extreme oxidizing property at room temperature limiting the use of ligand in reaction of complex formation.

5. Ligand

For high energy material ligand consisting of minimal number of C and H is required. It must also contain donor atom, usually N, O or S. In case of polydentate ligand, especially chelating ligands, great increase in stability of coordination compounds is observed.^[7]

Certain classes of organic compounds which can be used as ligand while designing explosive coordination compounds includes:

- i. Ammonia and its organic derivatives
- ii. Polydentate amines
- iii. Hydrazides of carboxylic acid^[10]

It could be concluded that design of high energy stable coordination compounds consists of searching the contradictory requirements like (i) reactivity of oxidizer and thermal stability of coordination compounds (ii) high enthalpy of formation of ligand and its basicity (iii) heat of explosion of coordination compounds with a given metal and chemical stability of coordination compounds under normal conditions.

6. Factors Effecting Burning Rate

Since redox transformation can be considered as the basis of combustion, the burning rate may be considered to depend on reactivity of:

i. Fuel Ligand: Composition of ligand influences fuel oxidizer ratio which in turns controls combustion temperature. Higher the combustion temperature higher more the burning temperature.

ii. Oxidizer anion: Nature of anion influences both heat of explosion and adiabatic flame temperature to large extent. In case of salts with oxidizing acids the anion reactivity may be estimated in terms of standard redox potential.^[11] The complexes of BrO_3^- , ClO_3^- , ClO_4^- anion oxidizer having greatest redox potential and respectively, the greatest reactivity, exhibit highest burning rate values. Order of explosives sensitivities of ammonium complexes $[\text{Co}(\text{NH}_3)_6](\text{OX})_3$ obtained: $\text{OX} = \text{NO}_3^- < \text{IO}_3^- < \text{NO}_2^- < \text{ClO}_4^- < \text{ClO}_3^- < \text{BrO}_3^- < \text{MnO}_4^-$ is consistent with the order of increasing redox potential of corresponding acids^[12]

iii. Metal atom induced in redox system: Increase in the metal atom mass results in the decrease of heat of explosion. The combustion temperature does not undergo significant variations, because a decrease in the heat of combustion with increasing metal atom mass is compensated by increase in the metal heat

capacity. Nature of metal effects burning rate to a large extent. Each anion oxidizer has been shown to possess its own set of metals, coordination compounds of which burn faster than salt of ligand and corresponding oxidizing acids.^[13]

7. Combustion Mechanism

Depending on the presence of metal atom taking part in redox conversion there could be various paths for the chemical process occurring during the combustion of coordination compounds. For anion having weak oxidizing properties, it may be suggested that ligand is oxidized by anion destruction products which are more reactive than anions. The initial stage of ligand oxidation in coordination compounds with non-oxidizable metals can be schematically represented by Fig. 1.

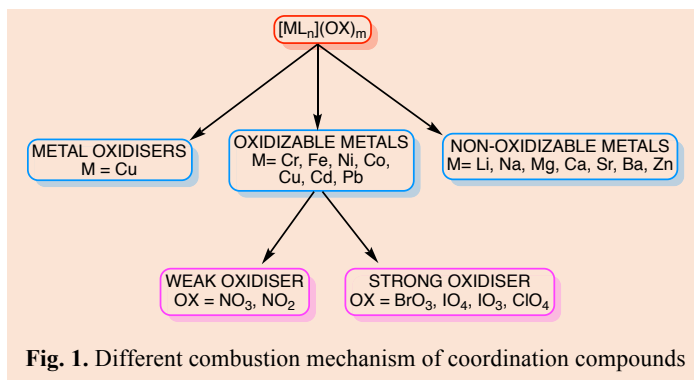
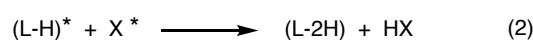
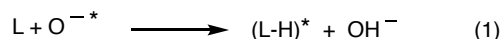


Fig. 1. Different combustion mechanism of coordination compounds

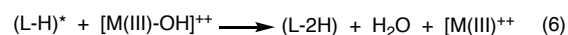
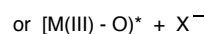
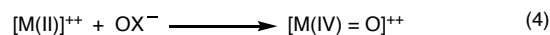
Scheme 1



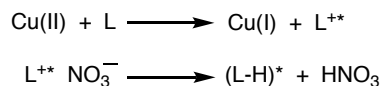
This cycle may further be repeated with X- and (L-2H) species. For metal atom showing variable valence state, the interaction between M(II) and anion in the combustion wave is considered to yield an oxygen-containing species, which may be depicted either as a complex M(III) with coordinated anion radical, $[\text{M}(\text{III})-\text{O}^*]^{2+}$, or as an oxocompound of metal(IV), $[\text{M}(\text{IV})=\text{O}]^{2+}$ ^[14-15]

Hence, the general mechanism is oxygen rebound from anion to ligand via metal oxo intermediate.

Scheme 2



According to mechanism proposed, only metals capable of forming high valent metal oxo species can produce the catalytic effect. The stronger the oxidative properties of anion, the larger the body of metals capable of the catalytic activity. For example, among perchlorate complexes even Cd(II) ($E^0 \text{ Cd}^{2+/3+} 3\text{V}$) exhibits catalytic activity, whereas for nitrate complexes only lead ($E^0 \text{ Pb}^{2+/4+} 1.7 \text{ V}$) can catalyze combustion. The catalytic effect like that observed for combustion of complex compounds of copper nitrate is characteristic of metals having oxidizing properties ($E^0 \text{ Cu}^{3+/2+} = 0.15\text{V}$). On reaction with Cu(II) followed by fast ligand oxidation by highly active metal-containing species occur in accordance to following reactions:



This results in appearance of strong oxidizer HNO_3 instead of weak oxidizer NO_3^- .

8. Conclusion

High energy explosives coordination compounds can be synthesized by:

- i. anion selection: defines explosive properties of coordination compounds, such as solubility, explosion temperature, explosive sensitivity, burning rate.
- ii. metal ion selection: determines the burning rate and largely chemical stability of coordination compounds.
- iii. ligand selection: defines heat of explosion of coordination compounds.
- iv. kinetics of redox reaction: determines the burning rate of coordination compounds

Synthesis and search of explosive coordination compounds is based on the knowledge of relationship between the burning rate level and structure of these compounds.

Author Information

Notes

The author declares no competing financial interest.

Biography



Dr. Surabhi Sinha is Assistant Professor in Department of Applied Sciences and Humanities (Engineering Chemistry) in United College of Engineering and Research, Prayagraj. She has completed her doctorate degree from University of Allahabad, Prayagraj in the year 2005. She has

number of publications in reputed journals to her credit. She is also recipient of several accolades and rewards.

References

1. S. G. Zhu, Y. C. Wu, W. Y. Zhang and J. G. Mu, *Propellants Explos. Pyrotech.*, **1997**, 12, 317-320.
2. A. V. Chernai, Sobolev, V. A. Chernai, M. A. Ilyushin, A. Dlugashek, *Combust. Explos. Shock Waves (Engl. Transl.)*, **2003**, 39(3), 335-339.
3. J. S. Chhabra, M. B. Talawar, P. S. Makashir, S. N. Asthana and H. Singh, *J. Hazard. Mater.* **2003**, 99, 225-239.
4. M. L. Lieberman, and J. W. Fronabarger, Proceedings of 7th International Pyrotechnic Seminar, July 1980, Colorado, **1980**, 322-55.
5. J. W. Fronabarger and M. L. Lieberman, Proceedings of 11th Symposium on explosives and pyrotechnics, **1981**, 38-1 to 38-14.
6. A. A. Grinberg, *Introduction in Chemistry of Coordination compounds*. Chimia, Leningrad, **1971**, 631.
7. *Engineering Design Handbook-Explosives Series: Properties of explosives of military interest*. The U.S Army Material Command Pamphlet No. 706-177, January **1971**, 187-90.
8. V. G. Ivanov, and G. L. Savinov, (*Russ. J. Phys. Comb. Explosion*), **1991**. 27(4), 18-24.
9. T. B. Joyner, *J. chem.*, **1969**, 47, 2729-30.
10. V. P. Sinditskii, V. I. Sokol, M. D. Dutov and A. E. Fogelzang, *Russ. J. Inorg. Chem. J.*, **1990**, 35(9), 2224-28.
11. A. E. Fogelzang, V. Ja Adzhemian and B. S. Svetlov, *Dokl. Akad. Nauk, SSSR*, **1971**, 199(6), 1296-98.
12. V. M. Latimer, The oxidation state of the elements and their potentials in aqueous solution, Prentice Hall, Englewood Cliffs, **1952**.
13. V. P. Sinditskii, A. E. Fogelzang, V. Egorshv, Yu; V. V. Serushkin, M. D. Dutov, and T. Y. Dutova, Proceedings of Zeldovich Memorial, September 1994, Moscow, **1995**, 747-61
14. I. I. Moiseev and M. N. Vergaftic, *Yspekhi khimii (Russ. Chem. Rev)*, **1990**, 39(12), 1931-59.
15. P. Collman, Brauman and B. Meunier, *J. Am. Chem. Soc.*, **1985**, 107(7), 2000-05.