

Synthesis and investigation the thermal behavior thermodynamically of new metal Complex of Cobalt nitrate

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ABSTRACT

Increasing the molecular accumulation and density of high-energy substances have a determinative role in improving the performance and intensity of energy release. Therefore, it is possible to increase the density of high-energy materials if the high-energy molecules can be arranged around a metal core as coordinated molecules. The aim of this project was to synthesize energetic complexes of cyclo molecules with Cobalt nuclei, cyclo molecule reacted with metal nitrate salts. To this purpose, cyclo was reacted with Cobalt nitrate with molar ratio of 1:4 in DMF solvent, respectively. To evaluate the ligand-to-metal ratio and characterize the structure of complex as well as to ensure proper complex synthesis, optical microscopy, UV-Vis spectroscopy, FT-IR spectroscopy and thermal gravimetric analysis (TGA) were used. The thermal decomposition process of the synthesized complexes compared to the pure cyclo showed that the cyclo coordinated to the central metals of nitrate intermediates, a two-step thermal decomposition process, converted to one step process. The energy released during the thermal decomposition process of Cobalt nitrate complexes is 649.3822 J/gr.

Keywords: Energetic complex; Copper (II) nitrate; Cobalt (III) nitrate; Iron (III) nitrate; Thermal gravimetric analysis

1. INTRODUCTION

High-energy materials are compounds that have high-energy bonds and are thermodynamically unstable. These include explosives, propellants and pyrotechnics with various applications [1]. Cyclotrimethylene trinitramine (RDX) is a high-energy explosive widely used as a staple element in solid propellants including rifles and rockets [2]. In the past

decades, many studies have been done on the combustion, decomposition and combustion behavior of RDX. Explosives produce heat through a process called oxidation release energy. Most strong explosives, including RDX, are oxygen-deficient compounds [3]. In order to have a more complete oxidation reaction, oxygen must be attached to high-energy materials.

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One practical solution is to incorporate an oxygen-rich compound with high-energy materials such as RDX, it is intended to form a mixture of high-energy materials, especially as this mixture increases the density of the molecule. One of the most important issues about high-energy materials is to increase their efficiency and improve their performance [5]. The performance of high-energy materials depends on various factors of which density has an important role, means that loading more moles of energy in a limited volume is better. Also, density is very important in the rate of wave propagation [6]. Researchers have reported two kinds of studies which show improvements in function: one, investigations that incorporate nitrate-containing functional groups into the main precursor structure using a new synthesis technique, and the other one is introduction of a metal intermediate group that improves performance. In the first category, Michel and his colleagues introduced a bunch of compounds into the explosive world that contained cyclic nitro-urea and had high density and performance. It is caused by a change in its precursor functional group [7]. Chavez and his colleagues investigated the synthesis and properties of 4,4-diamino-3,3-azofuran (DAAF) and the results showed that it had a density of 1.74 g / cm³ and a heat of formation of 106 kcal / mol [8]. Novikova and his colleagues synthesized and reported two substances 4,4-di-nitro 3,3-azoxy bis (furan) (DNABF) and 4,4-di-nitro 3,3-azobis (furan) (DNAzBF), which are high-energy-sensitive substances depend on shock [9]. These compounds have all been synthesized through the introduction of nitro or nitrate group into the precursor. The second category includes the investigation of the intermediate metal group effect. In this regard, Xing Cheng's research group synthesized and

investigated 16 compounds of high-energy ions of ferrocene compounds in order to investigate the effect of ferrocene compounds on thermal decomposition of solid propellants. All the compounds synthesized, exhibit high thermal stability and also have good catalytic effects on the thermal decomposition of ammonium perchlorate, HTPB, and the ratio of 1: 1 of these compounds. The synthesized compounds will have a relatively good catalytic effect for RDX material. Therefore, it can be proved that the presence of ferrocene groups on high-energy compounds can have a favorable effect and play an effective role [10]. In a research project carried out by the Jian-Jian Liu Group, a high-energy coordinated polymer with the closed formula structure $[Pb_2(C_5H_3N_5O_5)_2 (NMP)_n]$ was synthesized and its catalytic effect on the thermal decomposition of ammonium perchlorate, AP and RDX showed that this compound did not have a catalytic effect on RDX material but is a good catalyst for AP material in thermal decomposition. The research team of the Netherlands Faculty of Chemistry [11-12] investigated the energy properties of intermediate metal complexes. It should be noted that the only reported complexes are related to the nitrate or perchlorate complex of some intermediates with hydrazine and ethylene diamine. By comparing these compounds with each other, it was estimated that these complexes had sufficient power and energy to be used as explosives and also as standard explosives. Generally, two of the major modes of explosive modification are the creation of an energetic functional group in the target material or the placement of intermediates in the explosive core structure, some of which have been reviewed. In this research, attention has been paid to both methods simultaneously by using nitrate intermediate metals, both the number of

nitrate and nitro groups of the RDX material is altered and the addition of the intermediate metal to the main structure causes a major change in its performance. In this study, the focus is on the synthesis of a high-energy complex. To improve the performance of high energy RDX material, intermediate metal nitrate was used, which is an attempt to coordinate RDX into intermediate metal nitrate, which improves its properties. According to the widespread uses of high-performance materials in propellants and the importance of modifying their properties to promote performance and reduce prices, this project aims to synthesize a high-energy nitrate-mediated complex with high thermal performance.

2. DISCUSSION AND CONCLUSION

2.1-1 Job's Method for Determination of the Ligand to Metal Ratio of $Co(RDX)_4(NO_3)_3$

In order to investigate Job's method, the wavelength of the UV/Vis spectrophotometer was adjusted to the

wavelength corresponding to the maximum absorption of the complex which is at 243 nm and the absorption rate is measured for each sample synthesized at different concentrations. As the Cobalt (III) nitrate compound had a maximum absorption at 243 nm, the UV-Vis spectrum of the complex is the same. Table 1 shows the absorption spectra of samples synthesized from Cobalt (III) nitrate and RDX at constant wavelength of 243nm. According to the data from Table 1, Figure 1 is the Job's diagram as obtained by plotting the correct ratio of ligand to metal in the synthesis of high energy complex of Cobalt (III) nitrate and RDX with the ratio of 1:4 of $Co(NO_3)_3$ and RDX, respectively.

Table 1. Adsorption of Cobalt nitrate and RDX samples at 243 nm

adsorption	Molar ration
0.98	(1:4)S1
0.119	(1:2)S2
0.073	(1:5)S3
0.196	(1:6)S4

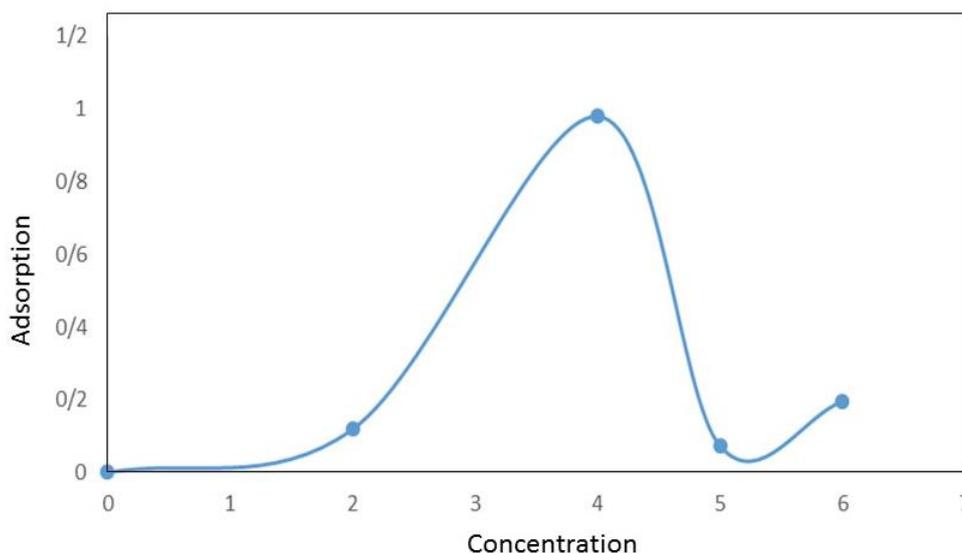


Fig. 1. The curve of the Cobalt nitrate and RDX sample curves.

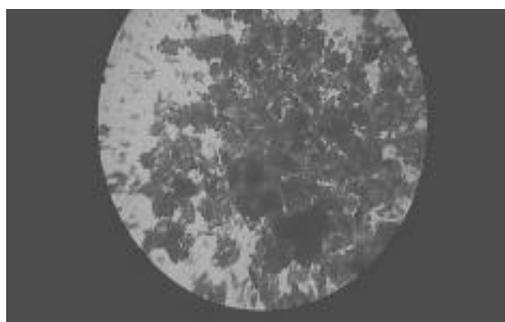
2.2. Investigation of high-resolution light microscope images of RDX and Cobalt nitrate in DMF solvent

The microscopic images of the samples containing Cobalt nitrate in 4 different molar ratios of 1:2 (S2), 1:4 (S1), 1:5 (S3) and 1:6 (S4) are shown as below. The microscopic image of the sample S2 in Figure 2a, shows that the amount of added RDX to this ratio is low for the reaction with Cobalt nitrate. In other hand, the resulting crystals are not uniform and show disunity, thus the ratio of 1:2 is not acceptable as the correct ratio. The resulting light microscopy images confirm the results obtained by the Jab method.

2.3. Investigation of FT-IR spectrum of $Co(RDX)_4(NO_3)_3$

Figure 3 shows the FT-IR spectrum of the RDX (a) and the resulting complex (b). As shown, all peaks of pure RDX material are

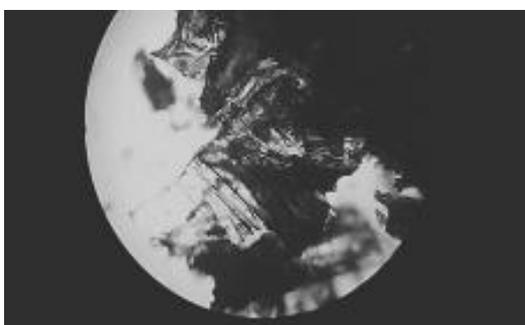
also present in the synthesized sample, which means the structure of the RDX material is not destroyed if it is in the complex structure. The only difference was a decrease in the vibration of the N-N transitions from 1270 to 1268.93 cm^{-1} and an increase in the NO_2 vibration from 1592 to 1592.91 cm^{-1} . In the case of the metal-nitrogen bond, the bond orders may vary, as was found for the metal-oxygen bond. For metal-nitrogen triple bonds, the stretching frequency may extend as high as about 1100 cm^{-1} . On the other hand, metal-nitrogen links with a bond order of one appear in the lower-frequency range of 200-300 cm^{-1} . These changes confirm the synthesis of the desired complex because the metal with RDX makes a complex from the N of ring, which reduces the N-N transitions to lower regions and raise the NO_2 transitions to higher one.



a) microscopic image S1



b) S2 microscopic image

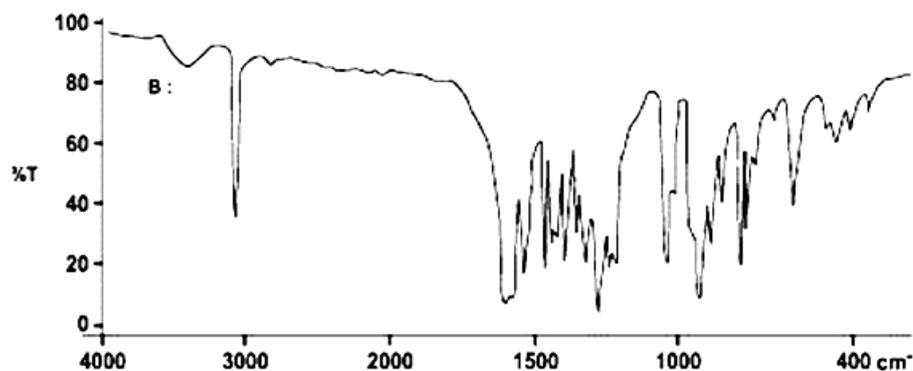


c) microscopic image S3

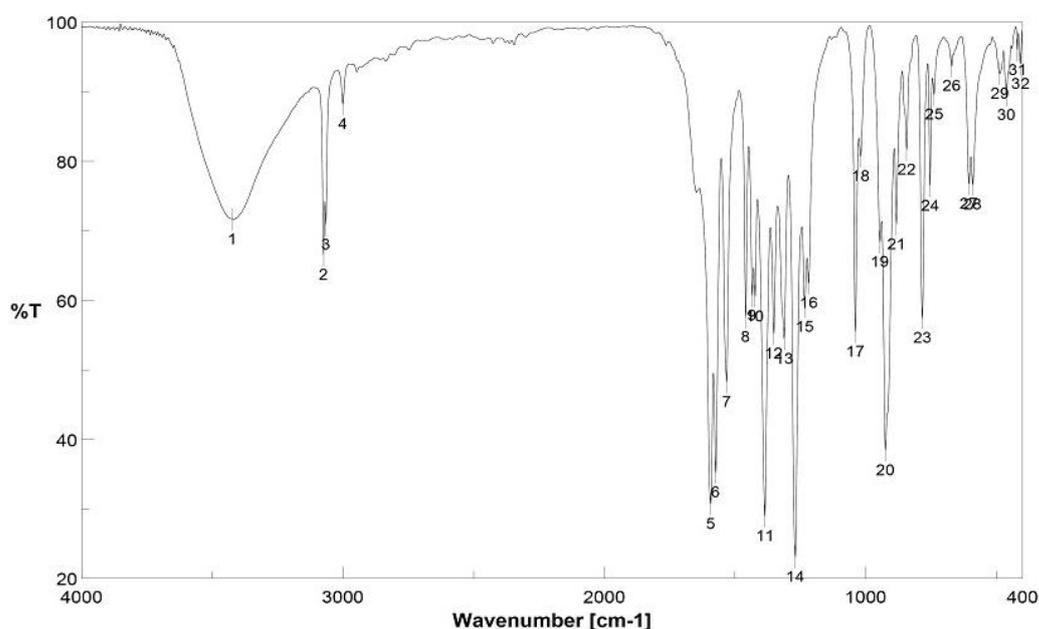


d) microscopic image S4

Fig.2. Microscopic images of samples synthesized at different molar ratios.



a) FT-IR spectrum of pure RDX



b) FT-IR spectrum of nitrate Cobalt complex and RDX in DMF

Fig. 3. Shows the FT-IR spectrum of complex and RDX.

2.4. XRD pattern of RDX

In the case of the metal-nitrogen bond, the bond orders may vary, as was found for the XRD pattern of a representative sample is shown Figure 4 along with the diffraction pattern for bulk-RDX. The XRD pattern of the bulk-RDX and nano-RDX showed the presence of numerous distinct peaks showing the crystalline nature of the samples. The crystal structure of RDX is well known to have at least 5 different polymorphs: a, b, g, d and e. The a-form is the most stable form at room temperature

(orthorhombic, $a=1.3182$ nm, $b=1.1574$ nm, $c=1.0709$ nm). The diffraction pattern of bulk-RDX matched well with the formed of RDX.

2.5. Thermal analysis test to investigate the thermal behavior of the samples

In this project, Differential scanning thermometry (DSC) analysis was used to study the thermal behavior of synthesized and pure RDX samples. This analysis enables quantitative measurement of sample enthalpy changes as a function of

temperature or time. Thermal analysis for the sample was carried out at a heating rate of 10 K / min at a temperature range of 25-400 °C. As shown in Figure. 5, the thermal analysis curve of TG and DSC is for pure RDX and also it is observed that the thermal decomposition process of pure RDX material is a two-step process. The first stage is the endothermic process at 197 °C. and the second is the exothermic process at 236 °C. The first step, the

endothermic phase, is not as desirable as a process related to high-energy compounds because the part of the heat given to the environment is absorbed by the particles which reduce the energy. The exothermic peak observed in pure RDX material has an intensity of -10.27 Mw. The heat released by RDX heat decomposition in the second stage is 350.0089 J/gr. Consequently, the higher the heat released, the more energy the material will have.

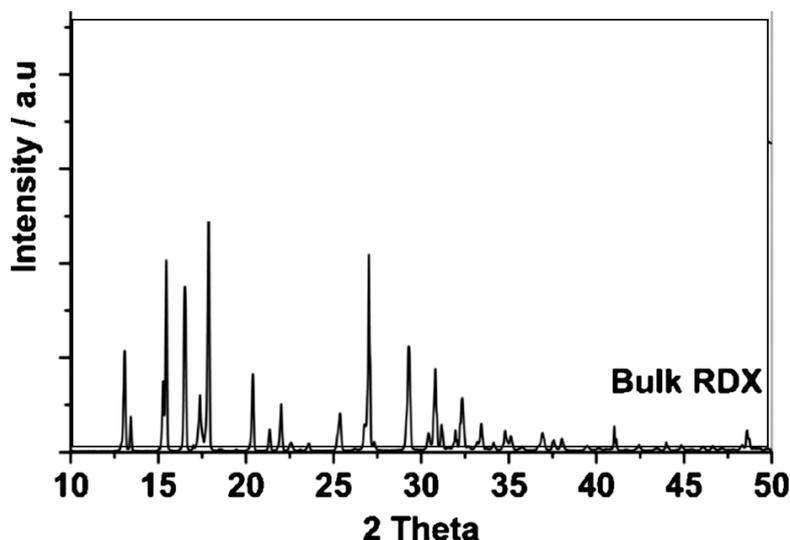


Fig. 4. The XRD pattern of RDX.

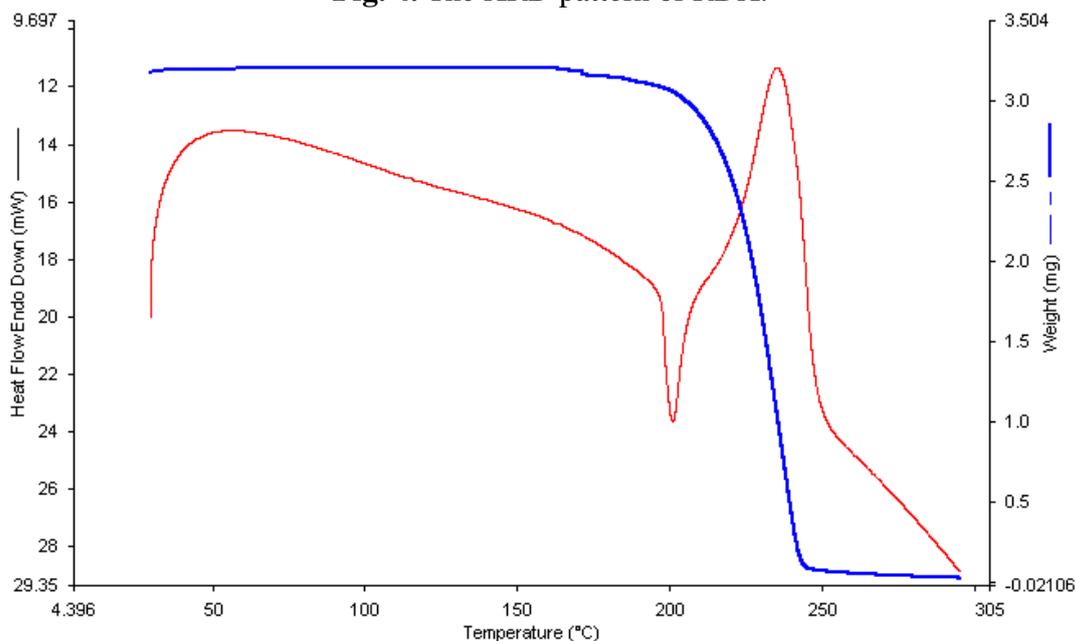


Fig. 5. thermal analysis curve of the complex synthesized of pure RDX in 10 k/min.

As shown in the Figure6, the process of thermal decomposition has changed dramatically relative to pure material. By comparing the respective curves with each other, it is clear that having a high-energy complex of RDX material and Cobalt nitrate, the endothermic peak of pure RDX material has been eliminated completely and the total energy of the material increases the system energy. Also, with keeping the temperature peak constant, it can be claimed that the synthesized material has good stability. The energy released from the thermal decomposition of the complex contains Cobalt nitrate and RDX is equivalent to 649.38226 J/gr which is approximately twice that of pure matter. In general, it can be said that the Cobalt nitrate material with three groups of nitrate and Cobalt metal, improves the thermal properties of purified RDX material, which eliminates all the failures of RDX material. Among the failures of pure RDX material compared to the

synthesized complex can be noted to: two-step process with one endothermic step, higher peak temperature as well as less released energy.

3. EXPERIMENTAL METHOD

3.1. Chemicals

In this study, RDX with molecular weight of 222gr.mol^{-1} prepared from industry and Cobalt (III) nitrate with molecular weight of 222gr. mol^{-1} and the DMF with purity in 98% purchased from Merck German Company were used as main precursors.

3.2. High energy complex synthesis method

The experimental procedure in this project consists of two parts. the first, to synthesize the energetic complex, initially 53.3 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as a nitrate source were transfer to a beaker contains 15 ml of DMF solvent and stirred by a magnet completely. Then, 88.8 g of RDX was added to the beaker and stirred until

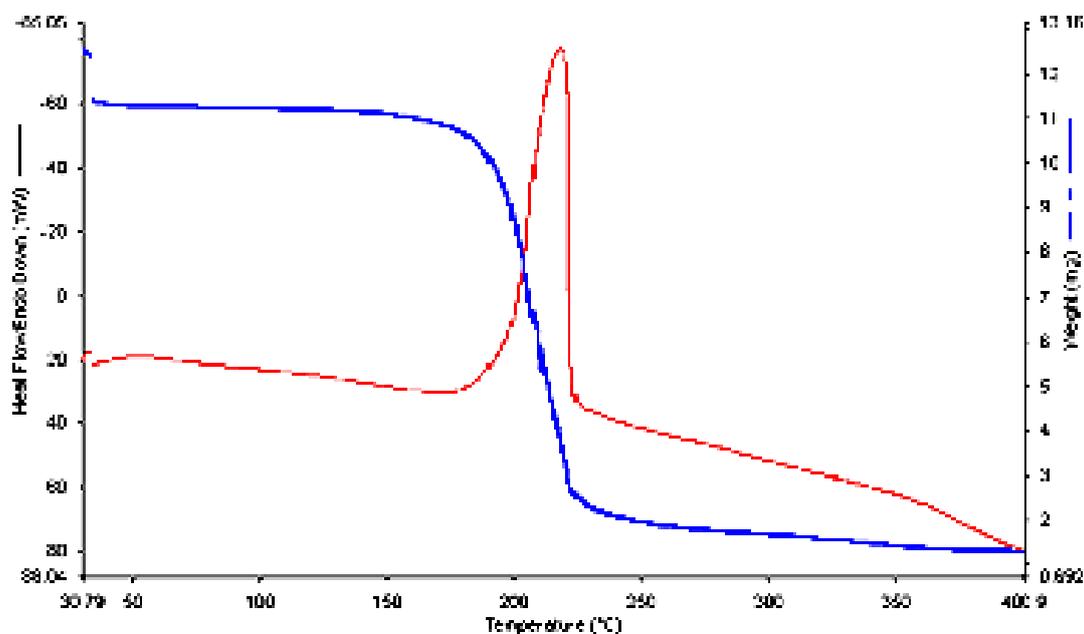


Fig. 6. shows the thermal analysis curve of the complex synthesized from RDX and Cobalt nitrate at a 1:4 molar ratios.

complete dissolution. After the materials dissolved completely, the beaker containing the obtained solution was kept in an electric oven at 80 °C for 4 days until the material was completely dried.

the second, experimental activities were synthesized in a number of different molar ratios to ensure the correct ratio of ligand to metal complexes and complementary studies were performed. For this purpose, the compounds were synthesized with 1:2, 1:4, 1:5 and 1:6 molar ratios and analyzed.

CONCLUSION

The high-energy complex is synthesized in a relatively simple and one-pot process that has unique properties including a single-step thermal analysis process without the endothermic step. This feature causes all the heat given to the sample increases the energy of the system. Also, because of the presence of metals in the compound structure and the addition of groups containing high-energy nitrogen bonds, the compound is explosive.

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