

A New Family of Energetic Complexes Constructed From Alkali Metals (K, Rb and Cs) and 7-Amino-4,6-dinitrobenzofuroxan: Crystal Structures, Thermal Decomposition Behaviors, Sensitivity and Catalytic Properties

¹Jian Cheng, ²Zuliang Liu, ¹Zhenming Li*, ³Yan Dong, ⁴Yu Zheng, ¹Rui Wang and ¹Li Sun

¹Department of safety science and engineering, Zhejiang University of Technology, Hangzhou, 310014, China.

²School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, 210094, China.

³Shijiazhuang No.4 Pharmaceutical Co.,Ltd., Shijiazhuang, 050021, China.

⁴School of Mechanical Engineering, Nanjing University of Science and Technology, Nanjing, 210094, China. lizmzf@163.com*

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Summary: This work reported a new family energetic complexes constructed from alkali metals (K, Rb and Cs) and 7-amino-4,6-dinitrobenzofuroxan (ADNBF). The crystal structures, thermal decomposition behaviors, sensitivity and catalytic properties of the novel materials were characterized by using X-ray diffraction, TG-DSC measurements and mechanical sensitivity tests. These crystals belonged to a triclinic and monoclinic system with space group $P-1$ and $P2_1/n$. ADNBF and complexes **1-3** exhibited one exothermic process with an exothermic peak temperature of about 265 °C, and the trend of thermal stability for ADNBF and complexes **1-3** was found to be in the order of $1 < 2 < 3 < \text{ADNBF}$. The trend in mechanical sensitivity for ADNBF and complexes **1-3** was shown to be in the order of $2 < 3 < 1 < \text{ADNBF} \approx \text{TNT}$. DSC measurements and analyses showed that the complexes **1-3** decreased the exothermic peak of the low-temperature decomposition (LTD) process of ammonium perchlorate (AP) by 66.3, 51.5 and 56.6 °C. Meanwhile the high-temperature decomposition (HTD) process of AP decreased by 38.1, 47.0 and 48.8 °C was observed. In addition, it was found that complexes **1-3** increased the overall heat of the HTD and LTD processes of AP by 405, 365 and 410 J/g, respectively.

Keywords: Energetic complex, 7-amino-4,6-dinitrobenzofuroxan, Crystal structure, Thermal decomposition behavior, Mechanical sensitivity, Catalytic property.

Introduction

Ammonium perchlorate (AP) is one of the most common oxidants in composite solid propellants, and the combustion behavior of AP-based propellants is sensitive to the ballistic modifiers, which can influence the pressure exponent and burning rate of the propellants [1-3]. For a long time, metals, metal oxides and complex oxides are commonly used as ballistic modifiers in AP-based propellants, which usually exhibit high catalytic activities [4]. However, the drawback of these traditional ballistic modifiers is, the increase in their concentration may decrease the total energy of the AP-based propellants, which is one of the most important performance parameters for the AP-based propellants. In order to overcome this disadvantage, synthesis of energetic ballistic modifiers with high performance is a hot research topic for the technological advancement of AP thermal decomposition [5-22].

Energetic ballistic modifiers are defined as energetic salts and complexes with high energy, low

sensitivity, high heat formation and high heat resistance, which have potential use as ballistic modifiers in AP-based propellants. From previous studies, a great number of new energetic ballistic modifiers were synthesized and characterized, and their catalytic activities on the thermal decomposition of AP have been fully evaluated in recent years [5-22]. Compared with traditional ballistic modifiers, energetic ballistic modifiers did not only lower the decomposition temperature, but also enhance the overall heat of thermal decomposition of AP. Although the energetic ballistic modifiers could increase the total energy of the AP-based propellants, however, the disadvantages also exist, such as containing high toxicity of heavy metal ions (lead, copper, nickel, etc), which inevitably cause serious threat to environment and human for their extreme toxicity. Therefore, developing of eco-friendly and energetic ballistic modifiers is of highly desirable, which would become a new research field for the technology of AP thermal decomposition.

*To whom all correspondence should be addressed.

As is well known, compared with heavy metal compounds, alkali metal compounds usually exhibited lower toxicity on human body and smaller pollution on environment [23]. Brill's work revealed that alkali salts of 3-nitro-1,2,4-triazol-5-one could be used as eco-friendly and energetic ballistic modifiers [24]. It was inferred that energetic alkali metal compounds could be employed as eco-friendly and energetic ballistic modifier in AP-based propellants. In our previous work, it was reported the synthesis, characterization, thermal decomposition behavior and catalytic properties of two alkali metal complexes (Na and K) of 5,7-diamino-4,6-dinitrobenzofuroxan (CL-14) [18, 25], which could be defined as eco-friendly and energetic ballistic modifiers. Based on that, this work aims to report a new family of eco-friendly and energetic ballistic modifiers (complexes **1-3**) constructed from alkali metals (K, Rb and Cs) and 7-amino-4,6-dinitrobenzofuroxan (ADNBF), which would exhibit an interesting, varied coordination mode in comparison to alkali metal complexes of CL-14 and the other energetic material-based metal complexes. The thermal decomposition behaviors and sensitivity properties of complexes **1-3** were investigated based on TG-DSC measurements and mechanical sensitivity tests. The catalytic performance of complexes **1-3** on the thermal decomposition of AP was also evaluated by DSC measurements and analyses.

Experimental

General caution

ADNBF and its coordination compounds are energetic materials and tend to explode under certain conditions. Appropriate safety precautions, such as safety glasses, face shields, leather coats and ear plugs, should be worn during the synthesis, testing and measurement processes, especially when prepared on a large scale and in dry state.

Materials and instruments

All reagents were analytic grade and used without further purification. The FTIR analyses were conducted with use a Bruker (55FT-IR) FTIR Spectrometer (500-4000 cm^{-1}). Elemental contents of carbon, hydrogen, and nitrogen were determined by a German Vario EL III analyzer. TG-DSC analyses were conducted on a TGA/SDTA851eMETTLER TOLEDO instrument from 25 to 500 °C.

Synthesis

ADNBF, ADNBF was prepared according to literature [26]. Anal. Calcd.(%):C, 27.89; H, 2.32; N, 32.54. Found: C, 27.77; H, 2.35; N, 32.75. IR, (KBr, cm^{-1}): 3382, 3285, 3075, 1611, 1582, 1501, 1474, 1415, 1352, 1302, 1249, 1071, 983, 813, 688, 625.

Synthesis of complexes 1-3. ADNBF (1.0 mmol) was added to a solution of MOH (where M=K, Rb, Cs, 1.0 mmol) in deionized water (20 ml) at 0-5 °C for 2 h, then filtered and washed with cool ethanol and air-dried. A yellow powder resulted with a 75-92.0% yield (based on ADNBF) and 0.1 g of this solid was dissolved in 10 ml of methanol. A crystalline product formed during slow evaporation of the solvent over a period of one week. Complex 1. Anal. Calcd. (%): C, 24.31; H, 1.01; N, 23.63. Found: C, 24.30; H, 1.02; N, 23.65. IR, (KBr, cm^{-1}): 3579, 3520, 3296, 3071, 1641, 1566, 1469, 1259, 1219, 1122, 992, 969, 915, 811, 777, 648. Complex 2. Anal. Calcd. (%): C, 21.08; H, 0.59; N, 20.49. Found: C, 21.09; H, 0.60; N, 20.47. IR, (KBr, cm^{-1}): 3586, 3518, 3300, 3076, 1647, 1566, 1457, 1321, 1246, 1220, 1117, 989, 913, 778, 641. Complex 3. Anal. Calcd. (%): C, 18.46; H, 0.77; N, 17.95. Found: C, 18.48; H, 0.78; N, 17.90. IR, (KBr, cm^{-1}): 3572, 3492, 3294, 3076, 1654, 1566, 1525, 1464, 1335, 1212, 1117, 989, 784, 648.

Sensitivity tests

The impact sensitivity and friction sensitivity measurements of the samples were conducted according to general methods [27].

Crystallographic data collection and structure determination

The crystal structures were determined on a Siemens (Bruker) SMART CCD diffractometer using monochromatic Mo-K α radiation ($\lambda=0.71073$ Å) at room temperature. All absorption corrections were performed by using the SADABS program [28]. Structures were solved by direct methods using the program SHELXL-97 [29]. All non-hydrogen atoms were located in difference Fourier maps and refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom, which they were bonded. A summary of the structural determination and refinement for complexes **1-3** were listed in Table-1.

TG-DSC measurements

Determination of the catalytic properties of complexes **1-3** (d_{50} : 5-15 μm), the AP (d_{50} : 4.5 μm) were conducted by dry mixing of each individual complex with AP (weight ratios 5:95) for 24 h. The resulted mixtures were then tested using DSC.

The specifications of TG-DSC measurements of ADNBF, complexes **1-3**, pure AP and AP mixtures were: sample mass, 0.5-1.0 mg; N_2 flowing rate, 25 cm^3/min ; heating rates (β), 2.5, 10 $^\circ\text{C}/\text{min}$; furnace pressures, 0.1 MPa; reference sample, $\alpha\text{-Al}_2\text{O}_3$; type of crucible, aluminum pan with a pierced lid.

Results and discussion

Structural description of complexes **1-3**

A summary of the analytical determinations and refinements for complexes **1-3** were listed in Table 1.

Complexes **1-2** were isostructural with the same triclinic $P-1$ space group and showed a 1D network. The structure of complex **1** was herein discussed. As shown in Fig 1(a), the asymmetric unit of complex **1** consisted of a monovalent potassium ion, one deprotonated ADNBF anion and a water ligand. At K1, the coordination environment was a distorted $\{\text{KO}_3\}$ coordination environment, defined by one oxygen atom from one N-oxide and two oxygen atoms from two nitro groups belonging to two other separate ADNBF ligands (K(1)-O(1)=2.777(2), K(1)-O(6)#1=2.793(3), K(1)-O(6)#2=2.871(3), symmetry code: #1: $-x+5/4, y,$

$-z+1/4$; #2: $x-1/2, -y+3/4, -z+1/4$). By contrast, the ADNBF⁻ ligand in complex **1** adopted an exotridentate $\mu_3\text{-k}^2\text{-O: O: O'}$ binding mode, connecting three K1 ions. The most intriguing structural feature in complex **1** was that two neighboring K centers were bridged by the oxygen atom from the nitro group water molecule (O6) in an approximately symmetric μ -mode with a bond angle of 127.15° to form the K-O-K chain along the a -axis (Fig 1 (b)). Furthermore, the neighboring K-O-K chains were connected by an oxygen atom from the N-oxide (O1) extending into a 1D network (Fig 1 (c)).

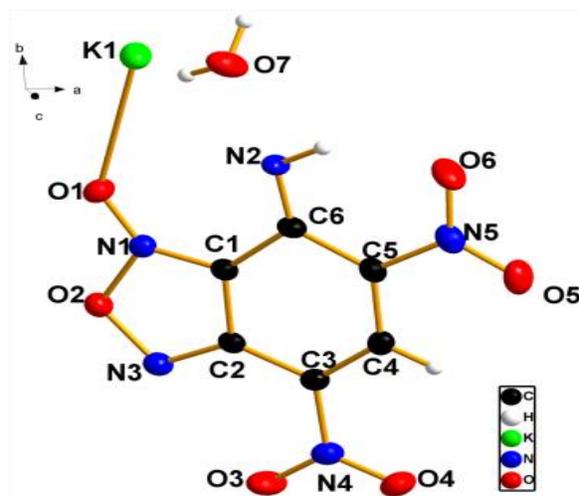
The single-crystal X-ray diffraction analysis revealed that complex **3** crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with an asymmetric unit consisting of one monovalent cesium ion, one deprotonated ADNBF anion and a bound water ligand (Fig 2(a)). The Cs1 atom was nine-coordinated by five oxygen donor atoms from five different ADNBF anions, two oxygen donor atoms from two different coordinated aqua molecules, two nitrogen atoms of two another ADNBF anions to give distorted CsN_2O_7 capped square antiprism geometries. On the other hand, the ADNBF⁻ ligand in complex **3** adopted an exotetradentate binding mode, connecting five Cs1 ions. The adjacent Cs(I) ions were bridged by ADNBF⁻ ligands to build a novel three-dimensional structure (Fig. 2(b)).

In accordance with our previous studies on metal complexes of CL-14 [18, 25], it could be deduced that the special coordination mode in these novel complexes might result in lower sensitivity and high heat resistance, which would be similar to those of Na and K complexes of CL-14.

Table-1: Crystal and experimental data of complexes **1-3**.

Complex	1	2	3
Empirical formula	$\text{C}_6\text{H}_5\text{KN}_5\text{O}_7$	$\text{C}_6\text{H}_5\text{RbN}_5\text{O}_7$	$\text{C}_6\text{H}_5\text{CsN}_5\text{O}_7$
CCDC number	945426	945358	945427
Formula weight	296.23	341.60	390.04
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P-1$	$P-1$	$P2_1/n$
$a/\text{\AA}$	4.5580(9)	4.6290(9)	10.630(2)
$b/\text{\AA}$	10.620(2)	10.735(2)	5.1770(10)
$c/\text{\AA}$	11.759(2)	11.702(2)	20.140(4)
α°	115.821(2)	114.73	90.00
β°	95.391(3)	95.36(3)	93.02(3)
γ°	91.705(3)	93.02(3)	90.00
$V/\text{\AA}^3$	508.55(17)	523.15(18)	1106.8(4)
Z	2	2	4
$D_{\text{calc}}/\text{g}\cdot\text{cm}^{-3}$	1.935	2.169	2.341
$F(000)$	298	332	740
Limits of data collection $^\circ$	$1.94 \leq \theta \leq 26.00$	$1.93 \leq \theta \leq 25.37$	$2.03 \leq \theta \leq 25.38$
Reflections collected	4004	1930	2028
Independent reflections (R_{int})	1971 (0.0303)	1930 (0.0000)	2028 (0.0000)
Goodness of fit	1.046	0.946	0.947
R indices ($I > 2\sigma(I)$)	$R_1 = 0.0514, wR_2 = 0.1456$	$R_1 = 0.0635, wR_2 = 0.1312$	$R_1 = 0.0638, wR_2 = 0.1503$
R indices (all data)	$R_1 = 0.0627, wR_2 = 0.1520$	$R_1 = 0.1146, wR_2 = 0.1511$	$R_1 = 0.1243, wR_2 = 0.1790$

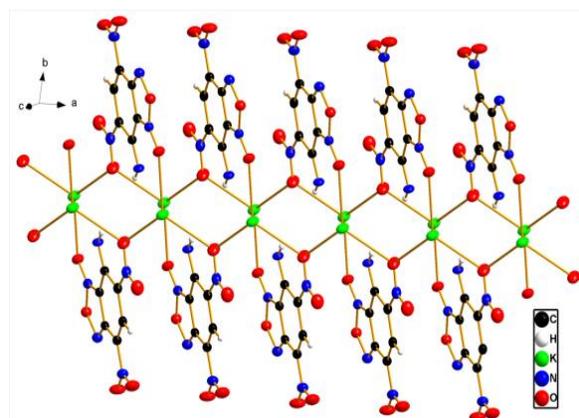
$$R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \quad wR_2 = \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}^{1/2}$$



(a)

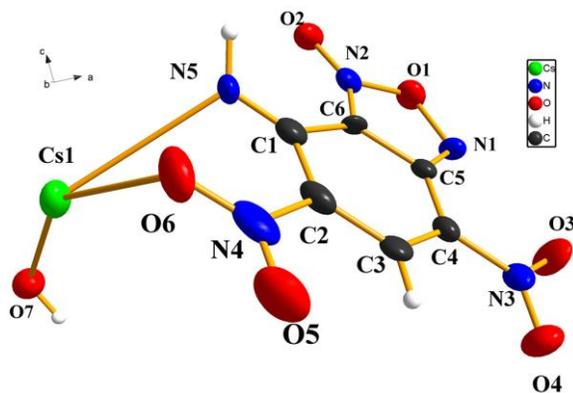


(b)

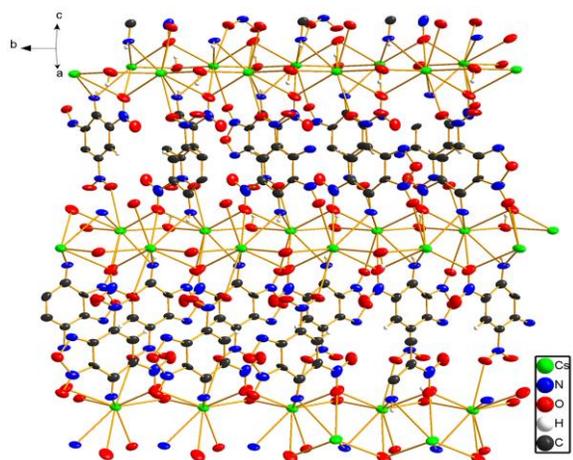


(c)

Fig 1: (a) ORTEP drawing of the asymmetrical unit of complex **1** with atomic labeling for metal ions and donor atoms. Displacement ellipsoids are drawn at a 30% probability level. (b) View of the K-O-K chain of complex **1** along the *a*-axis. (c) View of the 1D structure of complex **1**.



(a)



(b)

Fig 2: (a) ORTEP drawing of the asymmetrical unit of complex **3** with atomic labeling for metal ions and donor atoms. Displacement ellipsoids are drawn at a 30% probability level. (b) View of the 3D structure of complex **3**.

Sensitivity properties

The mechanical sensitivities of ADNBF and complexes **1-3** were determined and compared with RDX, TNT, tetryl, CL-14 and the alkali metal salts of CL-14 [27]. As shown in Table-2, the impact and friction sensitivity results for ADNBF, CL-14 and their alkali metal salts illustrated that the materials were low sensitivity energetic materials. The results also revealed that ADNBF and complexes **1-3** were insensitive to impact and friction, and a sensitivity trend was obtained in the order of $2 < 3 < 1 < \text{ADNBF} \approx \text{TNT}$. CL-14 and compounds **4-7** were impact and friction safe as well. However, the trend in sensitivity for these materials was found to be in the order of $\text{CL-14} < 4 < 5 < 6 < 7$.

Table-2: Sensitivity tests of the ADNBF and complexes 1-3

compound	Impact sensitivity(H ₅₀)/cm	Friction sensitivity/Kg
ADNBF	108	36
Complex 1	116	36
Complex 2	123	36
Complex 3	117	36
CL-14	129	36
Na salt of CL-14 (4)	75	36
K salt of CL-14 (5)	65	32.4
Rb salt of CL-14 (6)	42	28.8
Cs salt of CL-14 (7)	33	16.0
RDX[27]	35	12
TNT[27]	110	32.4
tetryl[27]	85	32.4

note: RDX: 1,3,5-trinitrohexahydro-1,3,5-triazine, TNT: 1,3,5-trinitrotoluene, tetryl: 2,4,6-trinitrophenylmethylnitramine.

Thermal decomposition behaviors

TG-DSC measurements were conducted to determine the thermal behaviors of ADNBF and complexes 1-3 (Fig 3). As shown in Fig 3, ADNBF and complexes 1-3 exhibited a rapid weight loss in the temperature range of 230.3-308.7 °C, and an exothermic peak temperature at 279.6, 261.9, 264.5 and 274.6 °C were also observed. These results indicated that ADNBF and complexes 1-3 were thermal stable energetic materials and a thermal stability trend for ADNBF and complexes 1-3 was in the order of 1<2<3<ADNBF.

Catalytic properties

Catalytic activities of complexes 1-3 on the thermal decomposition of AP

To explore the potential application of complexes 1-3 as ballistic modifiers in AP-based solid propellants, the catalytic effects of complexes 1-3 on the thermal decomposition of AP were determined by using DSC measurements and analyses (Fig 4 and Table-3). As shown in Fig 4, for pure AP, an endothermic peak was exhibited at 242.3 °C, which was probably due to crystal transition. The exothermic peaks at 330.2 and 432.5 °C could be attributed to the low-temperature decomposition (LTD) process and the high-temperature decomposition (HTD) process of AP. It was well established that LTD involved a heterogeneous process which included proton transfer in the AP subsurface to yield NH₃ and HClO₄. The capture of HClO₄ by proton trap ClO₃⁻ in the defect-bearing site of the lattice, and the decomposition of HClO₄. Alternatively, HTD was associated with the simultaneous dissociation and sublimation of AP to HClO_{4(g)} and NH_{3(g)} [30]. The DSC curves of AP with complexes 1-3 showed that the addition of complexes

1-3 had no obvious effect on the crystal transition temperature, but lead to significant changes in the decomposition patterns. The exothermic band of AP containing complexes 1-3 showed multiple broad and flat peaks, suggesting a complicated mechanism of decomposition. From Fig 4, the HTD of AP containing complexes 1-3 (394.4, 385.5 and 383.7 °C, respectively) was 38.1, 47.0 and 48.8 °C, which was lower than that of pure AP. The LTD of AP containing complexes 1-3 (263.9, 278.7 and 273.6 °C, respectively) was 66.3, 51.5 and 56.6 °C, which was also lower than that of pure AP. The overall heat of decomposition for the HTD and LTD processes of AP containing the complexes 1-3 was 405, 365 and 410 J/g, which was higher than pure AP. The results revealed that the thermal decomposition of AP was accelerated significantly by addition of complexes 1-3.

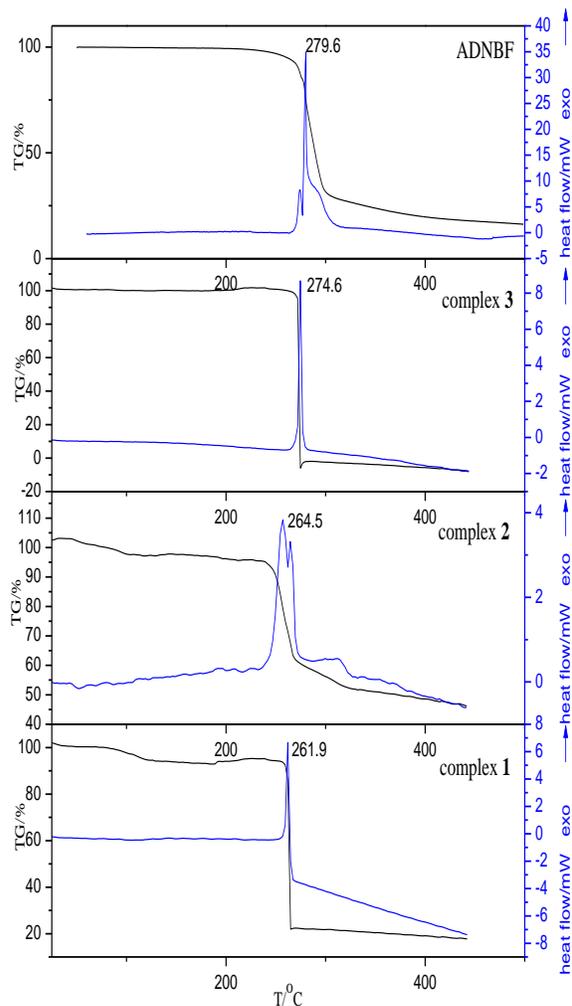


Fig. 3: TG-DSC curves of ADNBF and complexes 1, 2 and 3 at the heating rate of 2.5 °C/min.

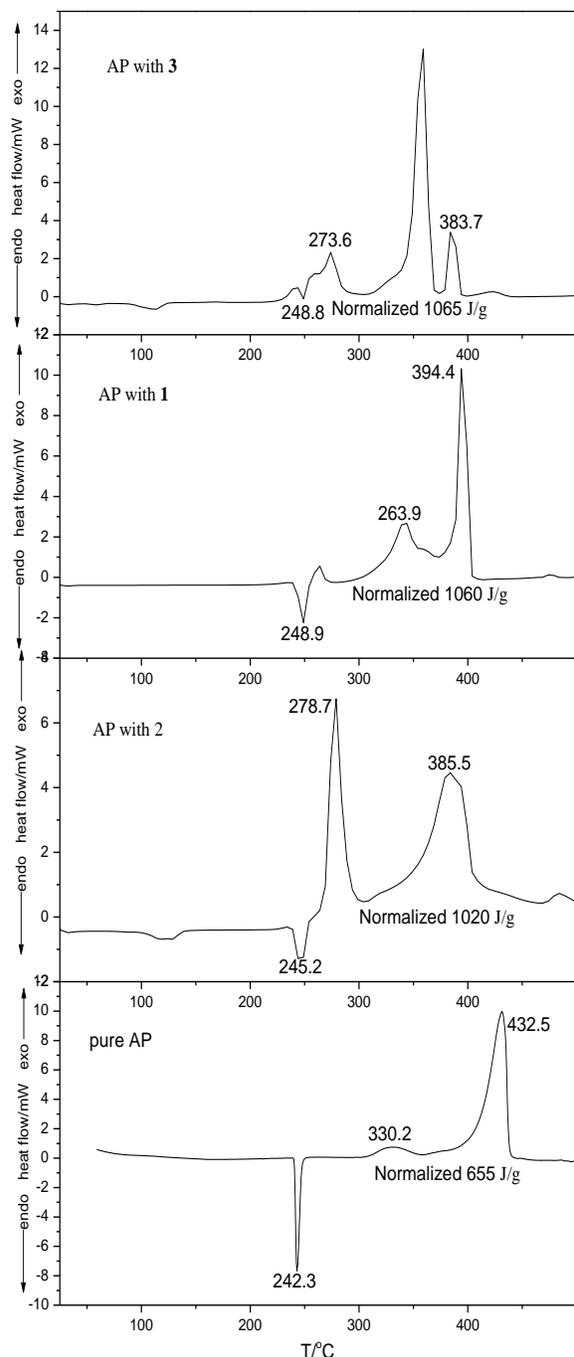


Fig. 4: DSC curves of pure AP and AP mixtures at the heating rate of 10 °C/min.

Table-3: Summary of DSC results for pure AP and AP with complexes 1-3 in LTD and HTD processes at the heating rate of 10 °C/min.

sample	$\Delta H/J/g$	T_p of LTD/°C	T_p of HTD/°C
Pure AP	655	330.2	432.5
AP with complex1	1060	263.9	394.4
AP with complex2	1020	278.7	385.5
AP with complex 3	1065	273.6	383.7

The catalysis reaction of AP with various ballistic modifiers (such as metals, metal oxides, complex oxides, energetic complexes and salts) has been fully studied in the literatures [4, 31, 32]. Metals, metal oxides and complex oxides exhibited higher catalytic activities on the thermal decomposition of AP when the decomposition temperature selected as the evaluation standard. Energetic additives exhibited higher catalytic activities when the decomposition heat was selected as the evaluation standard. However, all of the above ballistic modifiers have common disadvantages, that is, containing heavy metal ions, which results in environmental pollution in combustion process. In contrast, complexes **1-3** could effectively avoid the defect. In conclusion, complexes **1-3** could be used as eco-friendly and energetic ballistic modifiers in AP-based solid propellants.

Possible mechanism of thermal decomposition of AP catalyzed by complexes **1-3**

At present, the mechanism of the energetic additives on the thermal decomposition of AP has not fully understood yet in detail. Singh's work pointed out that the higher catalytic activity of the energetic additives on the thermal decomposition of AP might be attributed to the active metal oxides formed *in situ* in the system [10]. However, the experimental data consistent with this hypothesis was not provided. In our previous work, the catalytic reaction of AP with cobalt complex of 2,6-diamino-3,5-dinitropyrazine-1-oxide (Co-LLM-105) during thermal decomposition, as well as the decomposition mechanism of AP catalyzed by Co-LLM-105 were studied in detail [31]. The results showed that both components had catalytic effects on each other during the thermal decomposition process. The higher catalytic activity of Co-LLM-105 for the thermal decomposition of AP might be attributed to the fact that the active CoCO_3 , Co_3O_4 and CoO were formed *in situ*.

Base on the above results, it can be inferred that during the catalytic reaction of AP with complexes **1-3**, the complexes **1-3** could be decomposed at a lower temperature with the aid of AP, releasing a large amount of heat. This enhanced the total heat of the AP mixtures and generated the corresponding metal oxides *in situ* in the system, which might contribute to their catalytic effect on the thermal decomposition of AP. The possible decomposition pathway of AP with complexes **1-3** could be described as depicted in Fig. 5.

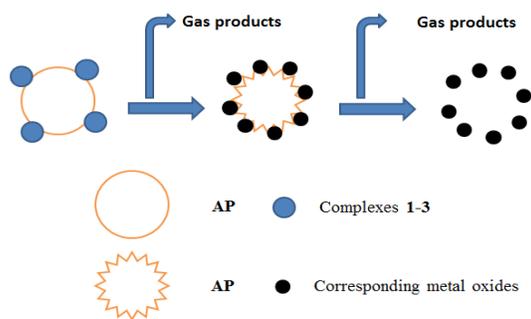


Fig. 5: Possible decomposition pathway of AP/complexes 1-3 mixtures.

Conclusions

In conclusion, this study reported a new family eco-friendly and energetic ballistic modifiers fabricated from alkali metals (K, Rb and Cs) and ADNBF. The crystals belonged to a triclinic and monoclinic system with space group $P-1$ and $P2_1/n$. ADNBF and complexes **1-3** exhibited one exothermic process with an exothermic peak temperature at 279.6, 261.9, 264.5 and 274.6 °C, respectively, and the trend of thermal stability for ADNBF and complexes **1-3** was found to be in the order of $1 < 2 < 3 < \text{ADNBF}$. The impact and friction sensitivity results for ADNBF and complexes **1-3** were 108, 116, 123, 117 cm and 36, 36, 36, 36 Kg, respectively, and the trend in mechanical sensitivity for ADNBF and complexes **1-3** was shown to be in the order of $2 < 3 < 1 < \text{ADNBF} \approx \text{TNT}$. DSC measurements and analyses showed that complexes **1-3** decreased the exothermic peak of the LTD process of AP by 66.3, 51.5 and 56.6 °C. Meanwhile, the HTD process of AP decreased by 38.1, 47.0 and 48.8 °C was also observed. In addition, it was found that complexes **1-3** increased the overall heat of the HTD and LTD processes of AP by 405, 365 and 410 J/g, respectively.

Acknowledgements

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