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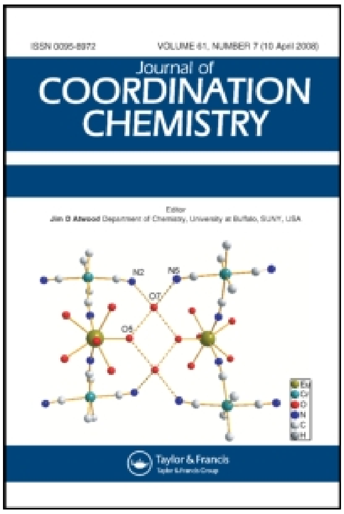

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Synthesis, structural characterization, and thermal properties of alkaline (earth) compounds derived from 2,4-dinitroimidazole

Guo-Fang Zhang[a]; Yong Wang[a]; Mei-Yu Cai[a]; Da-Min Dai[a]; Ke Yan[b]; An-Shan Ma[c]; Peng Chen[a]; Rui Wang[b]; Ping Li[a]; Jian-Hua Yi[d]; Feng-Qi Zhao[d]; Ji-Zhen Li[d]; Xue-Zhong Fan[d]
[a] Key Laboratory of Applied Surface and Colloid Chemistry (MOE), School of Chemistry and Materials Science, Shaanxi Normal University, Xi'an 710062, P.R. China [b] School of Computer Science, Shaanxi Normal University, Xi'an 710062, P.R. China [c] College of Mathematics and Information Science, Shaanxi Normal University, Xi'an 710062, P.R. China [d] Xi'an Modern Chemistry Research Institute, Xi'an 710065, P.R. China

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Synthesis, structural characterization, and thermal properties of alkaline (earth) compounds derived from 2,4-dinitroimidazole

GUO-FANG ZHANG*†, YONG WANG†, MEI-YU CAI†, DA-MIN DAI†,
KE YAN‡, AN-SHAN MA§, PENG CHEN†, RUI WANG‡, PING LI†,
JIAN-HUA YI¶, FENG-QI ZHAO¶, JI-ZHEN LI¶ and XUE-ZHONG FAN¶

†Key Laboratory of Applied Surface and Colloid Chemistry (MOE), School of Chemistry and Materials Science, Shaanxi Normal University, Xi'an 710062, P.R. China
‡School of Computer Science, Shaanxi Normal University, Xi'an 710062, P.R. China
§College of Mathematics and Information Science, Shaanxi Normal University, Xi'an 710062, P.R. China
¶Xi'an Modern Chemistry Research Institute, Xi'an 710065, P.R. China

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Eight alkaline and alkaline-earth compounds derived from 2,4-dinitroimidazole (2,4-HDNI) were synthesized and characterized by elemental analysis, FT-IR, and TG–DSC, of which K(2,4-DNI) (**1**), $Rb(2,4\text{-}DNI)(2,4\text{-}HDNI)(H_2O)_2$ (**2**), and $Ba(2,4\text{-}DNI)_2(H_2O)_4$ (**3**) were characterized by single-crystal X-ray diffraction analysis. All the three compounds were crystallized from water, but **1** was an anhydrate. The coordination number in **1** and **3** is 10, but in **2** is 9. The 2,4-DNI adopts either η^3, η^2, or η^1 coordination modes depending on the metal cation. In **3**, there is an inversion center located on the metal. Only in **2** does water play an important role for the construction of the structure; in **3** it is a hydrogen bonding participant. TG–DSC analyses of **1** were also performed, and non-isothermal decomposition reaction kinetics were obtained.

Keywords: 2,4-Dinitroimidazole; Main group metal compound; Crystal structure; Thermal behavior; Kinetics

1. Introduction

In modern ordnance there is a need to have an explosive molecule which is highly stable to thermal heating, substantially insensitive to impact, and highly powerful upon explosion. High-energy density materials (HEDMs) have several well-established characteristics including strained rings and cages, high nitrogen content, and high density and have, therefore, been studied worldwide [1]. High-nitrogen heterocyclic systems have long been recognized as a class of useful and promising structures for the design and synthesis of HEDMs [2]. A number of heterocycle-based energetic compounds were reported and used as high explosives and ingredients of propellants.

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*Corresponding author. Email: gfzhang@snnu.edu.cn

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Of these, polynitroimidazoles have attracted renewed attention due to their favorable insensitivity and explosive performance as well as improved safety characteristics [3]. 2,4-Dinitroimidazole (2,4-HDNI) serves as a good example. A few chemists have synthesized 2,4-dinitroimidazole and found it to be a highly promising insensitive HEDM [4]. Attractive features of 2,4-dinitroimidazole are its much less sensitivity than current high explosives (RDX and HMX), and it offers 15–20% more energy potential than insensitive explosive triaminotrinitrobenzene (TATB). Moreover, it can be prepared from the inexpensive starting materials.

Kinetic and thermodynamic characterization of chemical reactions is a crucial task in the context of thermal process safety as well as process development [5]. In brief, using modern thermal analysis techniques such as TG–DTG and DSC, the thermal behaviors of materials may be determined in a short time using milligram quantities. For the purpose of scale-up as well as kinetic and thermodynamic analysis of a desired decomposition reaction, non-isothermal reaction measurements are preferred.

We have prepared a number of metal salts derived from polynitropyridone and a few metal salts including Ni(II), Pb(II), and Sr(II) compounds derived from 2,4-dinitroimidazole and have characterized their structures by single-crystal X-ray diffraction analysis, and have studied their thermal behaviors and non-isothermal decomposition reaction kinetics [6]. In this article, we report the synthesis and characterization of eight alkaline and alkaline-earth metal compounds derived from 2,4-dinitroimidazole. Additionally, thermal analyses of TG–DTG and DSC of some compounds are discussed. Moreover, the decomposition reaction kinetics of one compound was investigated.

2. Experimental

2.1. *Materials and physical measurements*

2,4-Dinitroimidazole was synthesized according to the description in the literature [4b]. Other reagents are commercially available and used without purification. All experiments were carried out in twice-distilled water.

IR spectra of the complexes were recorded on a Perkin Elmer FT-IR spectrophotometer from 4000 to 400 cm^{-1} using KBr pellets. Elemental contents of carbon, hydrogen, and nitrogen were determined by a German Vario EL III analyzer. Crystal structures were determined with a Bruker Smart-1000 CCD diffractometer. The TG–DTG curves and DSC curves were obtained with a Model TGA 2950 thermobalance and a Model DSC 190S differential scanning calorimeter made by American TA Company. The conditions were sample mass, less than 1.00 mg; heating rate, 10°C min^{-1}; and atmosphere, flowing N_2 gas.

2.2. *Synthesis*

2.2.1. K(2,4-DNI) (1). To an aqueous solution of 2,4-dinitroimidazole (3.14 g, 20 mmol) at 60°C, equimolar KOH (1.12 g, 20 mmol) was added dropwise, and the yellow solution was stirred for another 1 h. The solution was then evaporated to dry and recrystallized from ethanol. Yield: 2.95 g (75.3%). Elemental analysis, Calcd (%): C, 18.37; H, 0.51; N, 19.93. Found (%): C, 18.67; H, 0.63; N, 18.36. FT-IR (KBr, cm^{-1}): 3112, m, ν_s(C–H); 1500, s, (C=C); 1473, s, $\nu_{as}(C–NO_2)$; 1432, s, ν_{as}(N–O); 1397, $\nu_s(C–NO_2)$; 1294, ν_s(N–O); 837, m, δ(N–O). Yellowish block-like crystals of **1** suitable for single-crystal X-ray diffraction analysis were obtained after 4 weeks by slow evaporation of its ethanol solution.

2.2.2. Rb(2,4-DNI)(2,4-HDNI)(H_2O) (2). A synthetic procedure similar to **1** was employed with Rb_2CO_3 instead of KOH. Yield: 3.77 g (45.1%). Elemental analysis, Calcd (%): C, 17.21; H, 1.20; N, 26.77. Found (%): C, 16.62; H, 0.812; N, 24.98. FT-IR (KBr, cm^{-1}): 3546, s, ν_s(N–H); 3372, s, $\nu_s(H_2O)$; 3112, m, ν_s(C–H); 1654, m, δ(HOH); 1503, s, (C=C); 1470, s, $\nu_{as}(C–NO_2)$; 1435, s, ν_{as}(N–O); 1391, $\nu_s(C–NO_2)$; 1299, ν_s(N–O); 831, m, δ(N–O). Yellowish block-like crystals of **2** suitable for single-crystal X-ray diffraction analysis were collected after 4 weeks by slow evaporation of its ethanol solution.

2.2.3. Ba(2,4-DNI)$_2$(H_2O)$_4$ (3). A synthetic procedure similar to **1** was employed with $Ba(OH)_2$. Yield: 3.23 g (61.8%). Elemental analysis, Calcd (%): C, 13.77; H, 1.93; N, 21.40. Found (%): C, 13.98; H, 1.87; N, 21.41. FT-IR (KBr, cm^{-1}): 3540, s, $\nu_s(H_2O)$; 3133, m, ν_s(C–H); 1621, m, δ(HOH); 1525, s, (C=C); 1481, s, $\nu_{as}(C–NO_2)$; 1443, s, ν_{as}(N–O); 1366, $\nu_s(C–NO_2)$; 1302, ν_s(N–O); 839, m, δ(N–O). Yellowish block-like crystals suitable for single-crystal X-ray diffraction analysis were collected after 2 weeks by slow evaporation of its ethanol solution.

Additionally, five other compounds, Li(2,4-DNI)(H_2O) (**4**), Na(2,4-DNI)(H_2O)$_2$ (**5**), Cs(2,4-DNI)(H_2O)$_2$ (**6**), Mg(2,4-DNI)$_2$(H_2O)$_6$ (**7**), and Ca(2,4-DNI)$_2$(H_2O)$_6$ (**8**), were prepared with similar methods and characterized by FT-IR spectroscopy and elemental analysis.

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2.3. *X-ray diffraction analysis*

A Single crystal of **1**, **2**, and **3** were coated with epoxy glue in order to prevent the spontaneous liberation of solvent molecules from the specimen under ambient conditions. Determination of the unit cell and data collection for the complexes were performed on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using φ and ω scans. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares with the Bruker's SHELXL-97 program [7]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogens were treated using a riding model. The details of data collection and the results of structure determination are summarized in table 1. Selected bond lengths and angles are presented in tables 2 and 3.

3. Results and discussion

3.1. *Preparations*

All alkaline and alkaline-earth compounds were readily prepared by the neutralization of 2,4-dinitroimidazole with the corresponding alkali hydroxides, carbonates, or oxides

Table 1. Crystallographic data for **1**, **2**, and **3**.

	1	**2**	**3**
Empirical formula	$C_3HKN_4O_4$	$C_6H_5N_8O_9Rb$	$C_6H_{10}N_8O_{12}Ba$
Formula weight	196.18	418.65	523.56
Temperature (K)	296(2)	296(2)	296(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
Unit cell dimensions (Å, °)			
a	6.887(3)	7.142(2)	17.279(2)
b	6.905(3)	7.187(2)	6.5225(8)
c	7.899(6)	13.345(4)	15.285(2)
α	98.987(6)	95.395(3)	90
β	97.690(6)	99.240(4)	110.7670(10)
γ	115.264(4)	92.085(4)	90
Volume (Å^3), Z	326.9(3), 2	672.2(4), 2	1610.8(4), 4
Calculated density (g cm^{-3})	1.993	2.068	2.159
Absorption coefficient (mm^{-1})	0.791	3.755	2.551
$F(000)$	196	412	1016
Crystal size (mm^3)	0.47 × 0.43 × 0.37	0.36 × 0.27 × 0.20	0.32 × 0.28 × 0.25
θ range for data collection (°)	2.68–24.97	2.85–25.50	2.85–25.50
Reflections collected	2014	4670	5365
Independent reflections	1120	2429	1493
Data/restraints/parameters	1120/0/109	2429/0/217	1493/0/124
Goodness-of-fit on F^2	1.086	1.023	1.062
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0442$, $wR_2 = 0.1316$	$R_1 = 0.0372$, $wR_2 = 0.0765$	$R_1 = 0.0242$, $wR_2 = 0.0644$
R indices (all data)	$R_1 = 0.0497$, $wR_2 = 0.1358$	$R_1 = 0.0593$, $wR_2 = 0.0860$	$R_1 = 0.0249$, $wR_2 = 0.0651$
Largest difference peak and hole (e Å^{-3})	0.350 and −0.340	0.356 and −0.332	0.357 and −0.995

(only for **8**) in aqueous solution. Since the products are highly soluble in water, we recrystallized the products in ethanol for easy isolation. Only the potassium compound (**1**) is anhydrous. All reactants were added in 1 : 1 stoichiometry, but the rubidium compound (**2**) crystallized with 1 : 2 stoichiometry as Rb(2,4-DNI)(2,4-HDNI)(H_2O), possibly due to the adsorption of carbon dioxide in air during the preparation and single-crystal growth forming rubidium bicarbonate, as observed in the crystallization of Rb[H(4DNPNO)$_2$] [6a].

3.2. *Descriptions of crystal structures of the compounds*

3.2.1. K(2,4-DNI) (1). Potassium 2,4-imidazolate (**1**) is anhydrous and crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the unit cell. The asymmetric unit contains one potassium cation and one 2,4-dinitroimidazole anion. Each potassium is 10-coordinate with seven ligands, of which one is η^3-ligand, one is η^2-ligand, and five are η^1-ligands (figure 1). The η^3-ligand coordinates to metal with one nitrogen of the imidazolyl ring and two oxygens of two nitro groups. The η^2-ligand links to K with one nitrogen of the imidazolyl ring and one oxygen of one nitro group. All five η^1-ligands bind the metal through one oxygen of one nitro group. The two K–N distances are 2.801(3) and 2.906(3) Å, comparable to those in [K(H_2TDA)H_2O]$_n$ and [K(H_2TDA)(H_3DTA)2H_2O]$_n$ (H_3DTA = 1,2,3-triazole-4,5-dicarboxylic acid), where the average K–N distance

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Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

K(2,4-DNI) (**1**)				Rb(2,4-DNI)(2,4-HDNI)(H_2O) (**2**)			
K(1)–O(3)$^{\#2}$	2.893(3)	K(1)–O(4)$^{\#1}$	3.091(4)	Rb(1)–N(5)	2.944(3)	Rb(1)–O(7)$^{\#3}$	3.274(3)
K(1)–N(2)$^{\#2}$	2.906(3)	K(1)–O(1)$^{\#5}$	3.290(4)	Rb(1)–O(4)$^{\#5}$	2.987(3)	Rb(1)–O(5)	3.439(3)
K(1)–O(1)	2.922(4)	K(1)–O(4)$^{\#6}$	3.346(4)	Rb(1)–O(3)$^{\#1}$	3.039(3)	Rb(1)–O(7)$^{\#4}$	3.494(3)
K(1)–O(2)$^{\#3}$	2.935(3)	K(1)–O(2)$^{\#1}$	3.382(4)	Rb(1)–O(9)$^{\#2}$	3.145(4)	Rb(1)–O(9)	2.860(3)
K(1)–N(1)$^{\#1}$	2.801(3)	K(1)–O(3)$^{\#4}$	3.074(4)	Rb(1)–O(8)	3.166(3)		
O(3)$^{\#2}$–K(1)–N(2)$^{\#2}$	56.14(9)	O(1)–K(1)–O(1)$^{\#5}$	86.01(10)	N(5)–Rb(1)–O(8)	51.55(7)	O(9)$^{\#2}$–Rb(1)–O(7)$^{\#3}$	58.58(8)
O(3)$^{\#2}$–K(1)–O(1)	66.67(9)	N(1)$^{\#1}$–K(1)–O(2)$^{\#1}$	50.62(8)	O(9)–Rb(1)–O(4)$^{\#5}$	73.95(9)	O(3)$^{\#1}$–Rb(1)–O(7)$^{\#4}$	56.33(8)
O(3)$^{\#2}$–K(1)–O(2)$^{\#3}$	91.89(10)	N(2)$^{\#2}$–K(1)–O(2)$^{\#1}$	77.58(9)	O(3)$^{\#1}$–Rb(1)–O(8)	58.49(7)	O(9)$^{\#2}$–Rb(1)–O(7)$^{\#4}$	63.28(7)
N(1)$^{\#1}$–K(1)–O(1)	109.85(10)	O(2)$^{\#3}$–K(1)–O(2)$^{\#1}$	61.37(10)	O(9)–Rb(1)–O(3)$^{\#1}$	92.32(9)	N(5)–Rb(1)–O(5)	49.15(7)
N(1)$^{\#1}$–K(1)–O(3)$^{\#4}$	95.26(10)	O(4)$^{\#1}$–K(1)–O(1)$^{\#5}$	64.10(10)	O(9)$^{\#2}$–Rb(1)–O(8)	75.87(8)	O(4)$^{\#5}$–Rb(1)–O(5)	60.64(7)
O(1)–K(1)–O(3)$^{\#4}$	64.78(10)	O(1)$^{\#5}$–K(1)–O(2)$^{\#1}$	85.04(8)	O(9)–Rb(1)–O(7)$^{\#3}$	69.11(8)	O(8)–Rb(1)–O(7)$^{\#4}$	80.22(7)
N(1)$^{\#1}$–K(1)–O(2)$^{\#3}$	92.23(10)	N(1)$^{\#1}$–K(1)–O(4)$^{\#1}$	54.16(9)	O(9)–Rb(1)–O(9)$^{\#2}$	87.33(8)	O(9)$^{\#2}$–Rb(1)–O(5)	85.66(7)
O(2)$^{\#3}$–K(1)–O(3)$^{\#4}$	64.18(9)	O(4)$^{\#1}$–K(1)–O(4)$^{\#6}$	90.13(10)	N(5)–Rb(1)–O(9)$^{\#2}$	70.55(7)	Rb(1)–O(9)–Rb(1)$^{\#2}$	92.67(8)
N(2)$^{\#2}$–K(1)–O(2)$^{\#3}$	69.66(9)	O(1)$^{\#5}$–K(1)–O(4)$^{\#6}$	50.16(8)	O(9)–Rb(1)–O(7)$^{\#4}$	58.26(8)	O(7)$^{\#3}$–Rb(1)–O(5)	53.80(7)
O(1)–K(1)–O(4)$^{\#1}$	55.71(9)	O(3)$^{\#2}$–K(1)–O(3)$^{\#4}$	85.51(10)	N(5)–Rb(1)–O(7)$^{\#3}$	86.19(8)	O(4)$^{\#5}$–Rb(1)–O(7)$^{\#3}$	67.15(8)

Symmetry transformations used to generate equivalent atoms for **1**: $^{\#1}x,y,z-1$; $^{\#2}x-1,y-1,z-1$; $^{\#3}-x,-y,-z-1$; $^{\#4}-x+1,-y+1,-z$; $^{\#5}-x,-y+1,-z-1$; $^{\#6}-x,-y+1,-z$; for **2**: $^{\#1}-x+2,-y,-z+2$; $^{\#2}-x+1,-y,-z+2$; $^{\#3}x,y+1,z$; $^{\#4}-x+1,-y-1,-z+2$; $^{\#5}x,y-1,z$.

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Table 3. Selected bond lengths (Å) and angles (°) for **3**.

Ba(1)–O(5)	2.847(2)	Ba(1)–N(1)$^{\#2}$	2.880(3)
Ba(1)–O(6)	2.858(2)	Ba(1)–O(4)$^{\#2}$	3.194(3)
Ba(1)–O(1)	2.862(3)		
O(5)–Ba(1)–O(5)$^{\#1}$	73.96(11)	O(5)$^{\#1}$–Ba(1)–N(1)$^{\#2}$	80.62(9)
O(6)$^{\#1}$–Ba(1)–O(6)	67.55(9)	O(1)–Ba(1)–N(1)$^{\#2}$	68.00(9)
O(5)–Ba(1)–O(1)	78.02(8)	O(1)–Ba(1)–O(4)$^{\#3}$	76.27(8)
O(6)$^{\#1}$–Ba(1)–O(1)	63.10(8)	N(1)$^{\#2}$–Ba(1)–O(4)$^{\#2}$	52.46(7)
O(6)–Ba(1)–O(1)	80.09(8)	O(6)$^{\#1}$–Ba(1)–O(4)$^{\#2}$	65.43(7)
O(5)–Ba(1)–N(1)$^{\#2}$	68.29(8)	O(5)$^{\#1}$–Ba(1)–O(4)$^{\#2}$	63.65(8)

Symmetry transformations used to generate equivalent atoms for **3**: $^{\#1}-x+1,y,-z+1/2$; $^{\#2}x+1/2,y-1/2,z$; $^{\#3}-x+1/2,y-1/2,-z+1/2$.

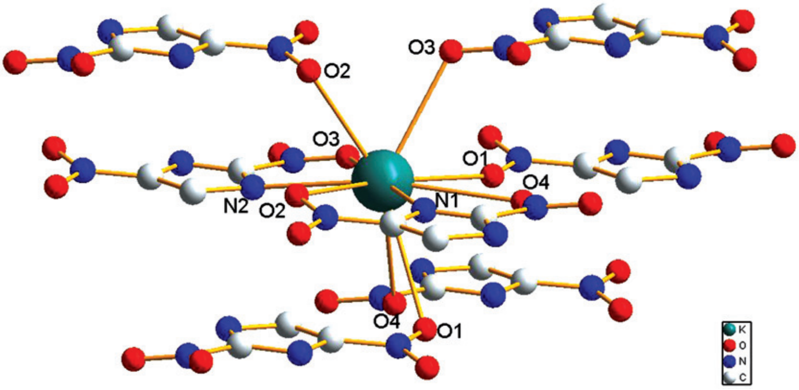

Figure 1. Ten-coordinate potassium cation of **1** showing the atom numbering scheme.

is 2.946(9) Å [8a]; the K–O contacts range from 2.893(3) Å (for O3$^{\#2}$) to 3.382(4) Å (for O2$^{\#1}$), slightly longer than those in compounds $[K(H_2TDA)H_2O]_n$, $[K(H_2TDA)(H_3DTA)2H_2O]_n$, and $8K_2L \cdot 11H_2O$ ($L = [(O_3S)_2C_6H_4]$) [8a, 8b]. Two $\pi\cdots\pi$ stacking interaction exists in this compound with the two imidazolyl rings (N1$^{\#4}$–C1$^{\#4}$–N2$^{\#4}$–C2$^{\#4}$–C3$^{\#4}$ and N1$^{\#3}$–C1$^{\#3}$–N2$^{\#3}$–C2$^{\#3}$–C3$^{\#3}$) contacting other two imidazolyl rings (N1–C1–N2–C2–C3 and N1$^{\#2}$–C1$^{\#2}$–N2$^{\#2}$–C2$^{\#2}$–C3$^{\#2}$), respectively, at a similar distance of Cg*–Cg$^{\#}$ = 2.464 Å. Figure 2 shows the coordination mode of one ligand with six potassiums. One nitro group adopts $\mu_2:\mu_2\text{–}\eta^1:\eta^1$ mode with potassium and another nitro group is linked to the metal in a $\mu_2\text{–}\eta^1:\eta^1$ mode.

The versatile oxygen bridges have important roles. The two-oxygen bridges (O2) and the four-oxygen bridges (O1 and O4) appear alternatively between adjacent potassiums resulting in a corrugated chain (figure 3). The K···K distances are 5.437(3) and 4.550(3) Å for the potassiums on both sides of two-oxygen and four-oxygen bridges, respectively. The corrugated chains are extended to a sheet by another type of two-oxygen bridge (O3) with a K···K distance of 4.383(3) Å, indicative of a stronger linkage of this two-oxygen bridge in comparison with the above two-oxygen bridge. Viewed down the *a*-axis, three kinds of oxygen bridges link six potassiums to form an

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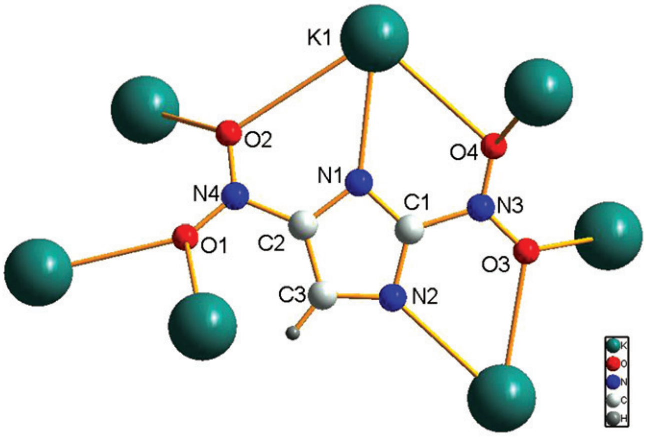

Figure 2. Coordination modes of 2,4-dinitroimidazole anion toward potassium in **1**.

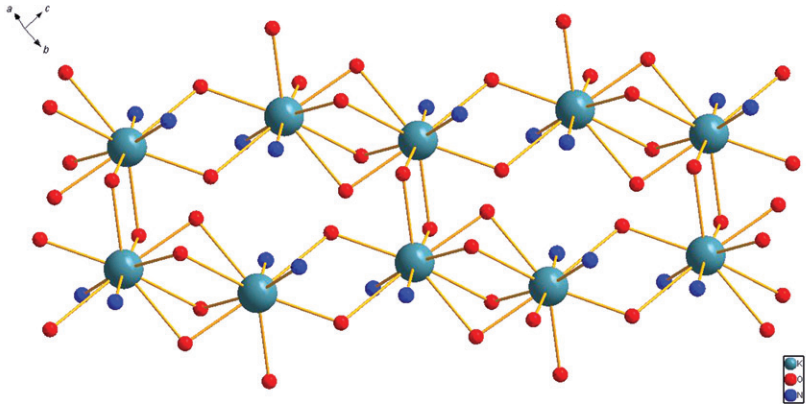

Figure 3. The extended array of **1** formed by oxygen bridges coordinated to potassium in the crystal. Only oxygens linked with cations are maintained for clarity.

irregular hexagon. The sheets are linked into a 3-D framework by both oxygens of the nitro groups and the nitrogen on imidazolyl rings of the 2,4-dinitroimidazole anions.

3.2.2. Rb(2,4-DNI)(2,4-HDNI)(H_2O)$_2$ (2). Compound **3** crystallizes in the triclinic space group *P-1* with $Z=2$. The asymmetric unit contains one rubidium cation, one neutral, and one anionic 2,4-dinitroimidazole as well as two water molecules. Each rubidium cation is nine-coordinate, linking to five ligands, three of which are anionic and two are neutral (figure 4). There exist different coordination patterns; one ligand adopts η^3 coordination through two oxygens of both nitro groups and one nitrogen of the imidazolyl ring, while the other four ligands link the metal by η^1 oxygen of the nitro group. The Rb–O distances cover a wide range from 2.987(3) Å for O4$^{\#5}$ to 3.494(3) Å for O7$^{\#4}$, and one Rb–O$_w$ bond (2.860(3) Å) is considerably shorter than

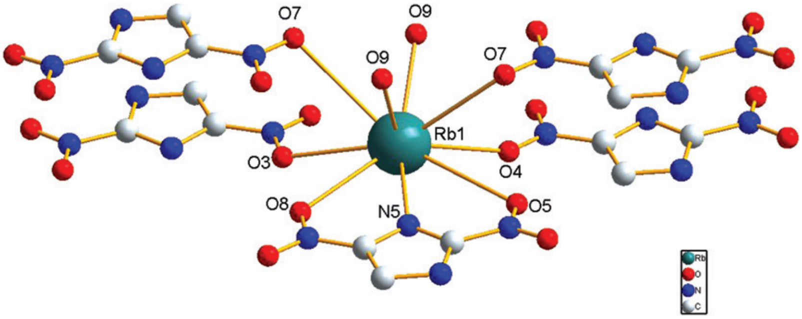

Figure 4. Nine-coordinate rubidium in **2** showing the atom numbering scheme.

Table 4. Hydrogen bonds and angles.

Compound	Atoms	Distances (Å)	Angles (°)
Rb(2,4-DNI)(2,4-HDNI)(H_2O) (**2**)	N(2)–H(2)...N(6)$^{\#6}$	2.767(4), 1.91	177.2
	O(9)–H(1W)...O(3)$^{\#7}$	3.305(4), 2.59	145.1
	O(9)–H(2W)...O(2)$^{\#7}$	3.434(4), 2.63	166.0
Ba(2,4-DNI)$_2$(H_2O)$_2$ (**3**)	O(5)–H(2W)...O(2)$^{\#5}$	3.036(4), 2.53	120.8
	O(5)–H(2W)...O(6)$^{\#6}$	2.855(4), 2.22	133.6
	O(6)–H(4W)...O(1)$^{\#1}$	2.993(4), 2.30	141.7
	O(5)–H(1W)...O(4)$^{\#7}$	3.317(4), 2.65	138.2
	O(6)–H(3W)...O(4)$^{\#3}$	3.283(4), 2.58	143.9
	O(6)–H(3W)...N(2)$^{\#8}$	2.915(3), 2.30	131.6

Symmetry transformations used to generate equivalent atoms for **2**: $^{\#6}-x+1,-y,-z+1$; $^{\#7}-x+2,-y+1,-z+2$; for **3**: $^{\#1}-x+1,y,-z+1/2$; $^{\#3}x-1/2,y-1/2,z$; $^{\#5}\ -x+1,-y,-z$; $^{\#6}x,y-1,z$; $^{\#7}-x+3/2,-y+1/2,-z$; $^{\#8}-x+1,-y+1,-z$.

another one (3.145(4) Å) (table 3). The coordination modes of the neutral and anionic ligands are different. The neutral one links two rubidium atoms with $\eta^1:\eta^1$ mode; while the anionic ligand coordinates to two metal centers with $\eta^3:\eta^1$ mode.

In assembling the structure, rubidium adopts a different linkage compared to its potassium analog. As shown in figure 5, the four oxygen bridges (two O9 and two O7) and the two $\eta^1:\eta^1$ O_{NO2} bridges (O3 and O4) appear alternatively between adjacent rubidiums forming a similar corrugated chain along the *c*-axis. The corrugated chains are extended to a sheet by another type of $\eta^1:\eta^1$ O_{NO2}-bridge (O7 and O8). The sheets are extended into a 3-D framework by hydrogen bonds: N(2)–H(2)$\cdots$N(6)$^{\#6}$, O(9)–H(1W)$\cdots$O(3)$^{\#7}$, O(9)–H(2W)$\cdots$O(2)$^{\#7}$ between water and imidazolyl rings as well as nitro group of the neutral ligands (table 4).

3.2.3. Ba(2,4-DNI)$_2$(H_2O)$_4$ (3). Crystals of barium 2,4-imidazolates (**3**) are monoclinic with the space group *C2/c*. The coordination environment of Ba(II) in **8** is isostructural to that of the Sr(II) in the strontium compound reported by us [6h]. Its asymmetric unit comprises of one barium cation and two 2,4-dinitroimidazole anions as well as four water molecules, as shown in figure 6. Each Ba(II) is 10-coordinate with two *O*,*N*-chelating and two *O*-monodentate ligands as well as four water molecules; there exists an inversion center located on barium. One 2,4-dinitroimidazole anion

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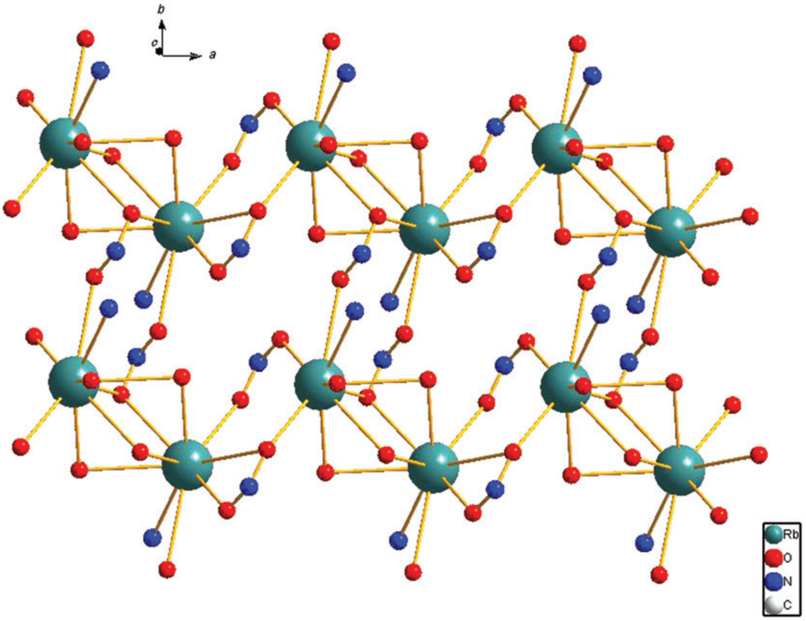

Figure 5. The extended array of **2** formed by oxygen bridges and nitro–O, O bridges to rubidium in the crystal. Only oxygens and nitro groups linked with Rb are maintained for clarity.

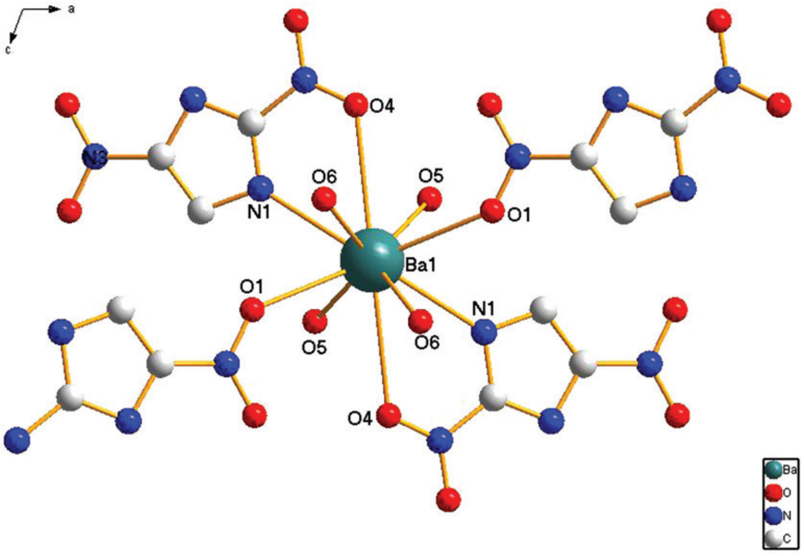

Figure 6. Ten-coordinate barium cation of **3** showing the atom numbering scheme.

coordinates to two metal cations. The Ba–O distances span a range from 2.847(2) Å for O5 to 3.194(3) Å for $O4^{\#2}$ and the Ba–N contact is 2.880(3) Å (table 3), a little longer than the corresponding Sr–O and Sr–N distances in $Sr(2,4\text{-}DNI)_2(H_2O)_4$ [6h] and much longer than those corresponding bond lengths in $Ca(PYDC)(H_2O)_4$ and $Ca(PYDC)_2(H_2O)_4$ (H_2PYDC = pyridine-2,3-dicarboxylic acid) [8c].

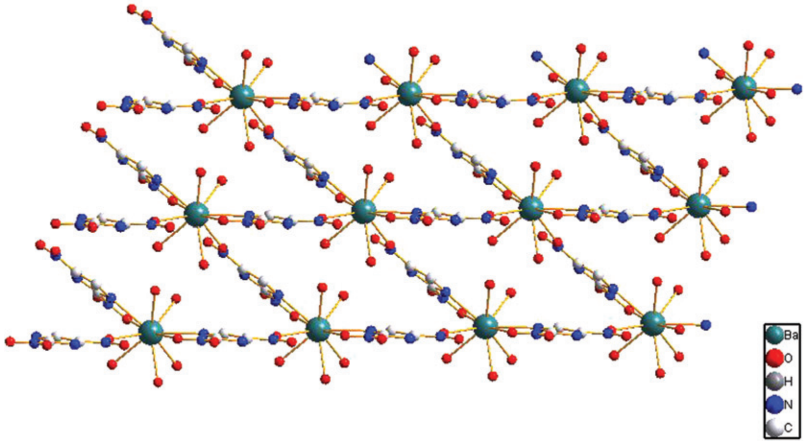

Figure 7. The extended array of **3** formed by 2,4-DNI anions coordinated to barium cations in the crystal. Only 2,4-DNI anions and atoms linked with Ba are maintained for clarity.

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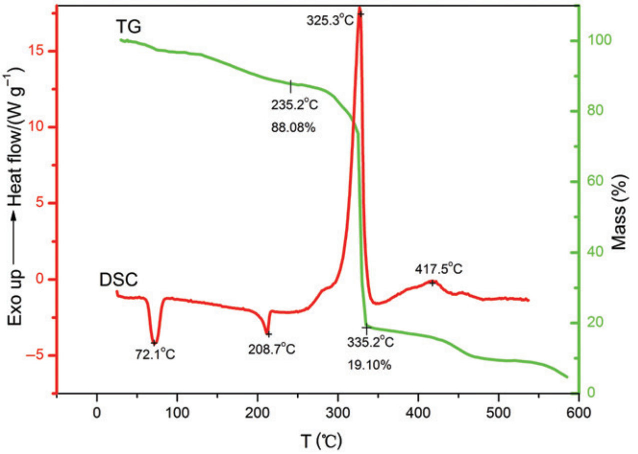

Figure 8. The TG–DSC curves for **1** at a heating rate of 10°C min^{-1}.

Along the *c*-axis, as shown in figure 7, the metals are linked by 2,4-dinitroimidazole anion to form 2-D sheets, which are further extended into a 3-D framework by rich hydrogen bonds between water and between water and the ligands (table 4), forming micro-channels along the *c*-axis.

3.3. *Thermal analysis*

In order to evaluate the thermal stability of the synthesized compounds, TG–DTG and DSC experiments were employed under N_2. Typical TG–DSC curves for **1** are shown in figure 8. The TG curve showed that the sample began to lose weight at 40°C and this weight loss continued up to 235°C with 11.9% mass loss, which could be due to the existence of small amounts of ethanol solvent in the sample. Correspondingly, the DSC curve shows two weak endothermic peaks (72.1°C and

208.7°C), the latter being due to the melting of the sample, consistent with the melting point of **1** (208.3°C). Then, **1** underwent a rapid weight loss (67.1%) from 243°C to 341°C with the loss of nitro groups and collapse of the imidazole ring backbone. Correspondingly, the DSC curve shows its first main exothermic process ($T_p = 325.3$°C), with heat release of $1.78 \times 10^3\,\mathrm{J\,g^{-1}}$ and then its second exothermic process occurred with $T_p = 417.5$°C, which might be ascribed to the further decomposition of the organic residues.

Additionally, the most probable mechanism of the main decomposition process of the potassium compound (**1**) and the corresponding kinetic parameters [apparent activation energy ($E_a\,\mathrm{kJ\,mol^{-1}}$), pre-exponential constant ($A\,\mathrm{s^{-1}}$)] as well as the most probable kinetic model function were studied (Supplementary material). The results showed that the reaction mechanism of the exothermal decomposition process of **1** is controlled by Mample Law with $n = 1/3$, $G(\alpha) = 3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$, and $f(\alpha) = [-\ln(1-\alpha)]^{1/3}$. E_a and A are $133.10\,\mathrm{kJ\,mol^{-1}}$ and $10^{9.49}\,\mathrm{s^{-1}}$, respectively. The corresponding kinetic equation of the decomposition reaction of **1** can be given as

$$\mathrm{d}\alpha/\mathrm{d}t = 10^{9.49}[-\ln(1-\alpha)]^{1/3} e^{-1.60\times 10^4/T}.$$

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4. Conclusions

We have synthesized a number of alkaline and alkaline-earth compounds derived from 2,4-dinitroimidazole. Potassium, rubidium, and barium compounds were characterized by single-crystal X-ray diffraction analysis showing that 2,4-DNI adopts various coordination modes depending on the metal cation. Only in rubidium compound (**2**) does neutral 2,4-HDNI participate in coordination. The structural determination also revealed that the coordination numbers in the three compounds are 9 or 10. The TG–DSC analysis was performed for **1** and its non-isothermal decomposition reaction kinetics were investigated. The kinetics of the main decomposition process of **1** showed that the kinetic model function in differential form, apparent activation energy, and pre-exponential constant of this reaction were $3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$, $133.10\,\mathrm{kJ\,mol^{-1}}$, and $10^{9.49}\,\mathrm{s^{-1}}$, respectively.

Supplementary material

CCDC-716886 (**1**), CCDC-716888 (**2**), and CCDC-716914 (**3**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk

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