Mechanochemical Conversion of Nano Potassium Hydrogen Terephthalate to Thallium Analogue Nanoblocks with Strong Hydrogen Bonding and Straight Chain Metallophilic Interactions

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Abstract

Irreversible mechanochemical conversion of three-dimensional K^I coordination polymer $[K(\mu_6\text{-HTA})]_n$ (**1**), [H_2TA = terephthalic acid], prepared by sonochemical procedure, to Tl^I analogue coordination polymer nanoblocks was studied. The structure of $[Tl(\mu_3\text{-HTA})]_n$ (**2**) is exactly the same as **1** and the Tl ion has distorted octahedral coordination. The carbonyl oxygen is coordinated to two different metal ions, while another oxygen atom is bonded to one metal and participates in a very strong hydrogen bond. Both compounds have secondary straight chain metallophilic interactions. In addition to the same structures of **1** and **2**, the same crystal data of them also approved that the chemistry of thallium(I) parallels that of the potassium(I) in many ways.

Keywords: Thallium(I); Coordination Polymer; Hydrogen Bonding; Thallophilic; Nano.

Introduction

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Extensive research has been devoted to the study of coordination polymers because of the variety of architectures and topologies¹ and potential applications in ion-exchange^{2,3}, sorption⁴, luminescence⁵, magnetism⁶, catalysis⁷, synthesis of nanomaterials⁸ and gas storage⁹. Compared with other materials with mononuclear nature, coordination polymers have particular structures, properties, and reactivities. It is possible to improve physical and chemical properties of CPs, by adjusting the nature and interactions among the individual components¹⁰. The design of crystalline architectures employing an understanding of the intermolecular interactions available to molecular subunits is the basis for crystal engineering, a key field straddling solid-state molecular assembly and structural analysis, whose importance lies in its capability for allowing control of crystal properties and functions as well as its structure¹¹. Much progress has been made using simple systems composed of covalent or strong hydrogen bond coordination compounds with peripheral hydrogen bonding substituents have been used to assemble infinite frameworks of one, two, and three dimensions^{12,13}. The new types of hydrogen bonds (HB) in organometallic chemistry can be divided into three types according to the site of coordination and the role of the organometallic species in a hydrogen bonded pair¹⁴. For one and two dimensional coordination polymers, weak interactions such as hydrogen bonds, electrostatic and Vander Waals interactions play important roles in stabilizing the assembled structures. Hydrogen bonds range from the very strong, comparable with covalent bonds, to the very weak, comparable with Vander Waals forces. Most hydrogen bonds are weak attractions with a binding strength about one-tenth of that of a normal covalent bond^{15,16}. Mechanochemical synthesis, reactions conducted by grinding solid reactants together with no or minimal solvent, has been demonstrated as an excellent technique for the formation of both organic and inorganic compounds^{17,18}. Mechanochemistry is viewed as an alternative approach to chemical synthesis and is not always considered when developing manufacturing processes of fine chemicals¹⁹. Coordination compounds with peripheral hydrogen bonding substituents can present

synthetic challenges to supramolecular chemists who are interested in hydrogen-bonded assembly, since the metal ions may themselves coordinate with the electronegative atoms that are sources of strong hydrogen bond donors and acceptors²⁰. In addition, the counter-ions that often escort metal complexes can serve as hydrogen bond donors or acceptors. Our aim was to focus on reversible/nonreversible structural transformations in thallium(I) coordination polymers by solid-state cation exchange process. Specially thallium(I) compounds are similar in structure and chemical properties to potassium which makes it easy for us to study their structural transformations in solid-state. This in this work we would like to study mechanochemical conversion of nano-structured $[\text{K}(\mu_6\text{-HTA})]_n$ (**1**) coordination polymer²¹, synthesized with sonochemical reaction, to $[\text{Tl}(\mu_3\text{-HTA})]_n$ (**2**), (H_2TA = terephthalic acid), also the reversibility of this solid-state conversion was studied. It is good to know that particle size and morphology of nanostructures depend on their synthesis method. For example, extensive research on synthesis of iron vanadate is being conducted using different techniques such as sol-gel²², wet chemical²³, microwave²⁴, hydrothermal²⁵, solid-state²⁶ and precipitation²⁷⁻²⁹. Among several different synthetic paths, many kinds of CPs have been prepared by sonochemical method³⁰. During ultrasonic process water gets pyrolyzed into OH and H radicals. Both radicals are very active and play important role in sonochemical reaction.²⁴ Ultrasonic irradiation is considered as a green energy source because of shorter reaction times and higher yields in comparison with thermal energy sources.³⁰

Experimental

Materials and Physical Techniques.

All reagents and solvents for the synthesis and analysis were commercially available and were used as received. The molecular structure plots were prepared using Mercury software³¹. PARSONIC 15S ultrasonic bath (with the frequency 28 KHz) was used for the ultrasonic irradiation. Melting points were measured on an Electrothermal 9100

apparatus and are uncorrected. IR spectra were recorded using an Equinox 55 FT-IR spectrometer (Bruker, Bremen, Germany) in ATR form, in the range of 400-4000 cm^{-1} with 4.0 cm^{-1} resolution and the 16 scan's numbers. Intensity data for $[\text{Ti}(\mu_3\text{-HTA})]_n$ (2) was collected with an Oxford Diffraction SuperNova CCD diffractometer using Mo-K_α radiation, the temperature during all data collections was maintained at 130.0(1) K using an Oxford Cryosystems cooling device. The structures were solved by direct methods and difference Fourier synthesis³². Thermal ellipsoid plots were generated using the program ORTEP-3³³ within the WINGX suite of programs³⁴. X-ray powder diffraction (XRD) measurements were performed using an X' Pert MPD diffractometer manufactured by Philips with monochromatized CuK_α radiation with scan rate of 0.02 degree per sec and simulated XRD powder patterns based on single crystal data were prepared using the Mercury software. The samples were characterized with a scanning electron microscope (Philips XL 30) with gold coating.

Synthesis of $[\text{K}(\mu_6\text{-HTA})]_n$ (1) nanostructures by a sonochemical process

To prepare nano-sized $[\text{K}(\mu_6\text{-HTA})]_n$ (1), 5 mmol (0.831 g) of the terephthalic acid (H_2TA) was dissolved in 15 ml methanol (A 0.33 M solution) and was mixed and stirred with solution of 5 mmol (0.280 g) KOH in 5 ml H_2O (A 1.0 M solution) at 100 °C for about 45 minutes and then this mixture was positioned in an ultrasonic bath. After 4 hours white precipitate was obtained which was filtered and dried at room temperature. d.p. = above 300 °C, yield: 0.791 g, 77.5 % based on final product.

Mechanochemical reaction of 1 with TiNO_3 in order to synthesis of $[\text{Ti}(\mu_3\text{-HTA})]_n$ (2).

This reaction was performed between 3.5 mmol (0.715 g) of $[\text{K}(\mu_6\text{-HTA})]_n$ (1) with 4.5 mmol (1.199 g) of TiNO_3 . These two reactants were mixed in mortar and ground up for 30 minutes through liquid-assisted grinding (LAG) method by adding a few droplets of

water. Then the mixture was four times washed with distilled water until the unreacted TiNO_3 and produced KNO_3 removed from it and the pure product was separated. d.p. = above 300 °C, yield: 1.091 g, 84.4 % based on final product.

Checking the reversibility of this solid state structural transformation with KNO_3

This reaction was performed between 1 mmol (0.369 g) of **2** with 1.5 mmol (0.150 g) of KNO_3 . These two reactants were mixed in mortar and ground up for 30 minutes through liquid-assisted grinding (LAG) method by adding a few droplets of water. The XRD pattern of resulting precipitate approved that this transformation is irreversible (Figure 1f in the SI) and in $[\text{Ti}(\mu_3\text{-HTA})]_n$ (**2**) was not converted back to **1** upon solid-state reaction with KNO_3 . Then the mixture was four times washed with distilled water until the unreacted KNO_3 removed from it and the pure phase of **2** was separated. d.p. = above 300 °C.

Synthesis of $[\text{Ti}(\mu_3\text{-HTA})]_n$ (2**) and preparation of its single crystals.**

1 mmol (0.166 g) of the terephthalic acid (H_2TA) was dissolved in 20 ml methanol (A 0.05 M solution) and was mixed and stirred with solution of 2 mmol (0.114 g) KOH in 5 ml H_2O (A 0.4 M solution) at 100 °C for about 45 minutes, then a solution of 2 mmol (0.532 g) TiNO_3 in 5 ml H_2O (A 0.4 M solution) was added to the mixture and the heating and stirring process was continued for about one hour. After filtering it was allowed to evaporate for several days and then suitable crystals were obtained. The crystals was separated and kept in its mother liquid. d.p. = above 300 °C, yield: 0.202 g, 54.7 % based on final product.

Results and discussion

The reaction between terephthalic acid (H_2TA) and KOH in ultrasonic bath resulted in formation of white powder which was dried at room temperature. A comparison between the XRD patterns simulated from single crystal X-ray data of potassium hydrogen terephthalate²¹ (Figure 1a) and that of the prepared powder (Figure 1b), approved the formation of $[\text{K}(\mu_6\text{-HTA})]_n$ (**1**) (Figures S1 in the SI and 2). HTA^- is bridging between six K ions and can be considered as hexadentate ligand (Figure S1a in the SI). J. A. Kaduk reported that in **1**, the K ion has distorted octahedral coordination (Figure S1a in the SI)²¹. The carbonyl oxygen O1 is coordinated to two different K, while O2 is bonded to one K and participates in a very strong hydrogen bond ($\text{O2}\cdots\text{O2}$ 2.46 Å, Figure S1b in the SI)²¹. There is a center of symmetry midway between the two O2 in the hydrogen bond²¹. Compound **1** is a three-dimensional coordination polymer with lozenge framework along the crystallographic c axis (Figure 2a) and has secondary straight chain $\text{K}\cdots\text{K}$ metallophilic interactions (Table 2) with distance of 3.77 Å which is lower than the sum of the vander Waals radii of two K atoms³⁵ (5.50 Å, Figure 2b). SEM image of the obtained powder approved that compound **1** micro and nanostructures were formed under ultrasonic irradiations (Figure 3a). Since thallium might be regarded as a relativistic alkali metal because Tl chemistry parallels that of the alkali metals in many ways³⁶ and the well-known toxicity of thallium compounds may also be associated with non-reversibility of the complexation reactions as compared to the action of potassium cations³⁷, we decided to study the structural changes of **1** during conversion of it to Tl(I) complex of HTA^- (**2**) by mechanochemical reaction of **1** with excess TlNO_3 . The XRD pattern of compound **1** after solid-state mechanochemical reaction with excess TlNO_3 (Figure 1c) approved that ion exchange process of K(I) with Tl(I) was occurred. After removal of KNO_3 and unreacted TlNO_3 from the products mixture, the pure phase of **2** (Figure 1d) was separated. SEM image of the mixture obtained from mechanochemical reaction of **1** with excess TlNO_3 indicated the formation of nanostructures (Figure 3b) with different morphology to **1** (Figure 3a). After washing the prepared mixture with

water, pure phase of compound **2** with nanoblock morphology was seen (Figure 3c). A comparison between the XRD patterns simulated from single crystal X-ray data of Tl(I) complex of HTA⁻ (**2**) (Figure 1e) and that of the prepared nanoblocks (Figure 1d), approved that the nanoblocks have the same structure as **2**. It should be noted that some differences between the peak intensity of simulated and experimental patterns is depending on textural features such as preferred orientations of nanocrystalline samples. Thus our attempts for synthesis of **2** from mechanochemical reaction of **1** with excess TlNO₃ is successful. In order to study the structure of **2** in detail, a reaction was done between H₂TA and TlNO₃ which provided crystalline materials of the general formula [Tl(μ_3 -HTA)]_n (**2**). Figure S2a (In the SI) shows the primary structural building unit of **2**. The structure of **2** is exactly the same as **1** and the Tl ion has distorted octahedral coordination (Figure S2b in the SI). The carbonyl oxygen O1 is coordinated to two different Tl ions, while O2 is bonded to one Tl and participates in a very strong hydrogen bond (O2...O2 2.47 Å, Figure S2a in the SI). There is a center of symmetry midway between the two O2 in the hydrogen bond too. Compound **2** is a three-dimensional coordination polymer with lozenge framework along the crystallographic c axis (Figures 4a and S3a in the SI) and has secondary straight chain Tl...Tl metallophilic interactions (Table 2) with distance of 3.76 Å which is lower than the sum of the vander Waals radii of two Tl atoms³⁵ (4.40 Å, Figures 4b and S3b in the SI). Against to those observed in thallium(I) compounds³⁸⁻⁴⁷, in compound **2**, the lone pair of Tl(I) is 'inactive' in the solid-state and the arrangement of O-atoms do not suggest a gap or hole in coordination geometry around the Tl(I) coordination sphere (Figure S2b in the SI). Our search also shows that Tl in compound **2** does not involve in Tl...C and Tl...H interactions.

The XRD pattern of **2** after mechanochemical reaction of it with KNO₃ (Figure 1f) is exactly the same as those observed in compound **2** (Figure 1d,e). Thus this transformation is irreversible. A comparison between crystal data of these two compounds (Table 1), shows that these two compounds have the same crystal system and

similar space groups, unit cell dimensions and volume too. Thus in addition to the same structures of **1** and **2**, the same crystal data of them also approved that the chemistry of thallium(I) parallels that of the potassium(I) in many ways. The SEM image of the prepared sample from the reverse reaction indicates the existence of compound **2** nanoblocks (Figure 3d). Thus its morphology does not change after grinding of it with excess KNO_3 . It should be also noted that compound **2** is a 3D coordination polymer (Figure 4) and its tendency to form 3D nanostructures like nanoblocks (Figure S2b-e in the SI), in addition to other factors, may be attributed to its crystal structure too. A comparison between the coordination geometry of the K and Tl atoms in the coordination polymers of **1** and **2** shows that during this solid-state cation exchange process, no structural changes in coordination mode of HTA^- and coordination sphere of K^+ and Tl^+ ions were occurred.

To further confirm of this irreversible solid-state reaction, IR spectra were recorded for all of five samples prepared during these conversion (Figure S4 in the SI). The IR spectrum of prepared powder of **1** under ultrasonic irradiation (Figure S4a in the SI) shows characteristic absorption bands for the HTA^- ligand. The absorption bands with variable intensity in the frequency range $1200\text{-}1500\text{ cm}^{-1}$ correspond to ring vibrations of the aromatic rings in HTA^- ligand. A comparison between the IR spectrum of compound **1** synthesized by sonochemical process (Figure S4a in the SI), compound **1** after solid-state mechanochemical reaction with excess TlNO_3 (Figure S4b in the SI), compound **2** after removal of KNO_3 and unreacted TlNO_3 from the products mixture (Figure S4c in the SI), IR spectrum of **2** after liquid-assisted mechanochemical reaction with KNO_3 (Figure S4d in the SI) and IR spectrum of the sample after removal of unreacted KNO_3 from the products mixture (Figure S4e in the SI) are exactly similar to each other which is due to the exactly the same structures of **1** and **2**. In none of each IR spectra, no weak broad band around $2800\text{-}3500\text{ cm}^{-1}$ was observed which indicated the existence of very strong hydrogen bonding interaction in **1** and **2** similar to the covalent O-H bonds.

TGA data (Figure 5a) indicated that **1** is stable up to 550 °C and did not show any mass loss up to this temperature. The thermal behavior of compound **1** after solid-state mechanochemical reaction with excess TiNO_3 (Figure 5b) is different from **1** (Figure 5a) which approved formation of other new compound (**2**) from this conversion. This TG curve shows that this sample is stable up to 365 °C. It seems that the observed mass loss of 21.8% (calcd 23.8% for pure phase of **2**) which accompanied with an exothermic peak at 398 °C may be attributed to removal of two CO_2 molecules from HTA^- of **2**. Figure 5c indicated that pure phase of **2** is stable up to 475 °C and the observed mass loss of 21.7% (calcd 23.8%) which accompanied with an endothermic peak at 525 °C may be attributed to removal of two CO_2 molecules from HTA^- ligand of **2**. A comparison between Figures 5b,c shows that impurity (like inorganic salts) can affect on thermal stability of our product. Here existence of unreacted TiNO_3 and produced KNO_3 decreases the thermal stability of **2** up to about 110 °C. Thermal behavior of compound **2** after mechanochemical reaction of it with excess KNO_3 was also examined (Figure 5d). The result is exactly the same as that obtained from mechanochemical reaction of **1** with excess TiNO_3 (Figure 5b). This observation also indicates that conversion of **1** to **2** is irreversible and in this stage we only have mixture of **2** and KNO_3 . Finally thermal behavior of compound **2** pure phase obtained after washing the mixture from previous stage was studied (Figure 5e). Its TG curve indicated that pure phase of **2** which obtained after mechanochemical treatment with KNO_3 is stable up to 355 °C. After this temperature, it showed two steps with observed mass losses of 7.1% (between 355-400 °C with an exothermic effect at 385 °C) and 11.2% (between 495-547 °C). Although the XRD pattern of this sample (Figure 1g) is exactly the same as **2** obtained from mechanochemical reaction of **1** with TiNO_3 (Figure 1d) and the XRD pattern simulated from single crystal X-ray data of **2** (Figure 1e), its thermal behavior (Figure 5e) showed some differences from pure phase of **2** synthesized from mechanochemical reaction of **1**

with TlNO_3 (Figure 5c). Probably mechanochemical grinding of **2** at final step affects on thermal stability of it.

Conclusions

In summary, irreversible solid-state structural conversion of three-dimensional K^{I} coordination polymer $[\text{K}(\mu_6\text{-HTA})]_n$ (**1**) synthesized by sonochemical procedure, to Tl^{I} analogue coordination polymer nanoblocks has been observed upon mechanochemical reaction of compound **1** with TlNO_3 . This irreversible exchange is similar to that occurred in biological systems approved the toxicity of thallium. The structure of $[\text{Tl}(\mu_3\text{-HTA})]_n$ (**2**) is exactly the same as **1** and the Tl ion has distorted octahedral coordination. The carbonyl oxygen is coordinated to two different metal ions, while another oxygen atom is bonded to one metal and participates in a very strong hydrogen bond. Both compounds have secondary straight chain metallophilic interactions. Against to those observed in thallium(I) compounds, in compound **2**, the lone pair of $\text{Tl}(\text{I})$ is 'inactive' in the solid-state and the arrangement of O-atoms do not suggest a gap or hole in coordination geometry around the $\text{Tl}(\text{I})$ coordination sphere. In addition to the same structures of **1** and **2**, the same crystal data of them also approved that the chemistry of thallium(I) parallels that of the potassium(I) in many ways. The IR spectra of them no weak broad band around $2800\text{-}3500\text{ cm}^{-1}$ was observed which indicated the existence of very strong hydrogen bonding interaction in **1** and **2** similar to the covalent O-H bonds. Studying these types of solid-state mechanochemical reaction is being investigated in our laboratory.

Supplementary material.

Complete bond lengths and angles, co-ordinates and displacement parameters have been deposited at Cambridge Crystallography Data Center. Supplementary data are available

from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 1565856 for compound **2**.

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Table 1. Crystal data and structure refinement for compounds **1** and **2**.

Identification code	2	1
Empirical formula	C ₈ H ₅ O ₄ TI	C ₈ H ₅ O ₄ K

Formula weight	369.49	204.22
Temperature	130.01K	298
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	C 2/c	C2/c
Unit cell dimensions	a = 18.8490(10) Å b = 3.7564(2) Å c = 11.3409(6) Å $\alpha = 90.00^\circ$ $\beta = 96.888(6)^\circ$ $\gamma = 90.00^\circ$	a = 18.825(4) Å b = 3.7700(8) Å c = 11.179(2) Å $\alpha = 90.00^\circ$ $\beta = 94.56(3)^\circ$ $\gamma = 90.00^\circ$
Volume	797.19(7) Å ³	790.9(3) Å ³
Z	4	4
Density (calculated)	3.079 g.cm ⁻³	1.715 g.cm ⁻³
Absorption coefficient	20.234 mm ⁻¹	0.645
F(000)	664	416
Crystal size	0.349 × 0.324 × 0.265 mm ³	0.42 × 0.1 × 0.04 mm ³
Theta range for data collection	4.4680 to 35.7190 °	
Index ranges	-17 ≤ h ≤ 24 -4 ≤ k ≤ 4 -14 ≤ l ≤ 14	0 ≤ h ≤ 18 -3 ≤ k ≤ 3 -10 ≤ l ≤ 10
Independent reflections	884	376
Absorption correction	Multi-scan	None
Data / restraints / parameters	918 / 0 / 61	367 / 1 / 72
Goodness-of-fit on F ²	1.078	1.018
Final R indices [I > 2σ(I)]	R ₁ = 0.0390 wR ₂ = 0.1006	R ₁ = 0.0302 wR ₂ =
R Indices (all data)	R ₁ = 0.0401 wR ₂ = 0.1013	R ₁ = 0.0455 wR ₂ = 0.0715
Ref.	This work	21

Table 2. Selected bond lengths /Å and angles /° for compounds **1** and **2**.

Compound 1	(This work)	Compound 2	(Ref. 21)
Tl(1)-Tl(1)	3.7564(2)	O(1)- K- O(1)	96.22(13)
Tl(1)-O(1)	2.786(5)	O(1)- K- O(1)	177.39(11)
O(1)-Tl(1)-Tl(1)	129.89(10)	O(1)- K- O(1)	86.39(7)
O(1)-Tl(1)-O(1)	100.2(2)	O(1)- K- O(1)	91.00(12)
O(1)-Tl(1)-Tl(1)	50.11(10)	O(1)- K- O(2)	98.91(8)
Tl(1)-Tl(1)-Tl(1)	180.0	O(1)- K- O(2)	112.64(8)
		O(1)- K- O(2)	80.03(8)
		O(1)- K- O(2)	66.82(8)
		O(1)- K- O(2)	112.64(8)
		O(1)- K- O(2)	98.91(8)
		O(2)- K- O(2)	132.31(15)
		O(1)- K- K	48.11(6)
		O(1)- K- K	134.50(6)
		O(2)- K- K	113.84(7)
		O(1)- K- K	45.50(6)
		O(2)- K- K	66.16(7)
		O(1)- K- K	131.89(7)
		K-K-K	180.0

Figure captions:

Figure 1. XRD patterns; a) simulated pattern based on single crystal data of compound $[\text{K}(\mu_6\text{-HTA})]_n$ (**1**), b) compound **1** nanostructures synthesized under ultrasonic irradiations, c) compound **1** after mechanochemical reaction with excess TiNO_3 , d) pure phase of $[\text{Ti}(\mu_3\text{-HTA})]_n$ (**2**), e) simulated pattern based on single crystal data of compound **2**, f) compound **2** after mechanochemical reaction of it with excess KNO_3 , g) pure phase of **2**.

Figure 2. a) A fragment of three-dimensional coordination polymer in $[\text{K}(\mu_6\text{-HTA})]_n$ (**1**) with lozenge framework along the crystallographic c axis and b) illustrating secondary straight chain $\text{K}\cdots\text{K}$ interactions in **1** with purple dashed line along the crystallographic a axis, (K = purple, O = red, C = gray and H = white, in part b H atoms have been omitted for clarity).

Figure 3. SEM images of a) $[\text{K}(\mu_6\text{-HTA})]_n$ (**1**) nanostructures synthesized under ultrasonic irradiations, b) compound **1** after mechanochemical reaction with excess TiNO_3 , c) pure phase of $[\text{Ti}(\mu_3\text{-HTA})]_n$ (**2**), d) compound **2** after mechanochemical reaction of it with excess KNO_3 , e) pure phase of **2**.

Figure 4. a) A fragment of three-dimensional coordination polymer in $[\text{Ti}(\mu_3\text{-HTA})]_n$ (**2**) with lozenge framework along the crystallographic c axis and b) illustrating secondary straight chain $\text{Ti}\cdots\text{Ti}$ interactions in **2** with purple dashed line along the crystallographic a axis, (Ti = orange, O = red, C = gray and H = white, in part b H atoms have been omitted for clarity).

Figure 5. Thermal behaviour of a) $[\text{K}(\mu_6\text{-HTA})]_n$ (**1**) nanostructures synthesized under ultrasonic irradiations, b) compound **1** after mechanochemical reaction with excess TiNO_3 , c) pure phase of $[\text{Ti}(\mu_3\text{-HTA})]_n$ (**2**), d) compound **2** after mechanochemical reaction of it with excess KNO_3 , e) pure phase of **2**.

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