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Development of a Lean Process to the Lead-Free Primary Explosive DBX-1

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Jerry S. Salan^{*‡}*

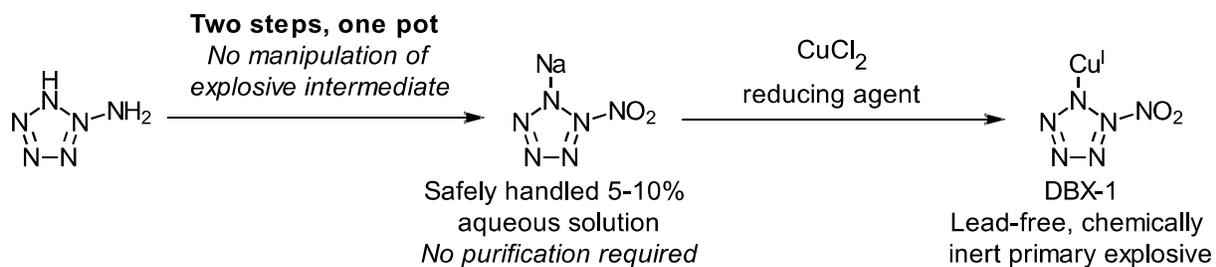
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3 ABSTRACT: Copper(I) 5-nitrotetrazolate (DBX-1) has emerged in recent years as a primary
4 explosive that could serve as a replacement for lead azide (LA), a widely used explosive that has
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ABSTRACT: Copper(I) 5-nitrotetrazolate (DBX-1) has emerged in recent years as a primary explosive that could serve as a replacement for lead azide (LA), a widely used explosive that has fallen out of favor due to its toxicity and chemical compatibility issues. While there is a significant amount of interest in this material, the development of DBX-1 has been hampered by the tedious and poorly understood chemical process for its preparation. To consistently produce DBX-1, two explosive intermediates must be isolated, and one of them requires purification. In this article, we present an improved process for the synthesis of DBX-1. In this process, neither of these intermediates needs to be handled by an operator, and the purification step is no longer necessary. It would be practical to perform the entire process under remote control, a necessity for energetic material manufacturing. We discuss the implications of our findings for the development of a robust process for the reproducible production of high quality DBX-1.

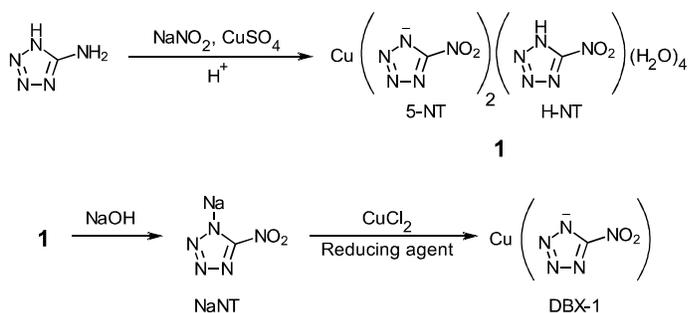
KEYWORDS: Primary explosives, lean manufacturing, hazardous process

Introduction

In military and commercial blasting, the explosive chain reaction is typically initiated by detonation of a small quantity of highly sensitive primary explosive. The sensitive nature of these primary explosive allows for larger charges of relatively insensitive high explosives to be detonated using a small, targeted stimulus. Two of the most widely used primary explosives are lead(II) azide (LA) and lead(II) styphnate.¹ In recent years, concerns have been growing that lead contamination in air and soil, particularly in military training grounds and firing ranges, poses a significant threat to the safety of personnel working in these areas, and to the environment as well.² In addition to the environmental drawbacks, LA is also problematic because the azide anions can react with moisture in the presence of carbon dioxide to generate hydrazoic acid, a toxic and explosive low-boiling liquid.³ Azide can also form extremely sensitive explosive complexes with other metals, such as copper. The unintended formation of copper azides in aging munitions with copper detonator shells has led to fatal accidents as bomb investigators and explosive ordinance disposal teams attempted to move these items.⁴

For these reasons, much effort has been focused on the development of minimally toxic and chemically inert primary explosives that might serve as substitutes for LA.⁵ A breakthrough came in the discovery of copper(I) 5-nitrotetrazolate (DBX-1), a primary explosive that can serve as a “drop-in” replacement for LA in existing detonator designs.⁶ This material has comparable properties to LA as an explosive, but does not have the toxicity and compatibility drawbacks that LA suffers from.⁷ In spite of this, DBX-1 has made little progress in replacing LA since its discovery. The major factors slowing adoption of DBX-1 are associated with its production. A highly reproducible protocol for preparing DBX-1 will be necessary for this material to be used widely in commercial blasting products and military ordinance items.

DBX-1 is prepared from sodium 5-nitrotetrazolate, NaNT (Scheme 1), a compound that has been used as a precursor to other explosives produced on large scale, including tetraamine-*cis*-bis(5-nitrotetrazolato)cobalt(III) perchlorate (BNCP),⁸ and mercuric nitrotetrazolate.⁹ The synthesis of NaNT was first disclosed by von Herz in 1937.¹⁰ In von Herz's procedure for the preparation of NaNT, 5-aminotetrazole (5-AT) is first converted to 5-nitrotetrazole (5-NT) by means of a Sandmeyer reaction. The product precipitates from the reaction mixture as **1**, a copper(II) complex sometimes referred to as the 'acid copper salt' of 5-NT. Von Herz reported its composition as Cu(H-NT)(NT)₂(OH)₂. This material is isolated as a gelatinous green solid that is isolated by a tedious filtration. In 1978, Gilligan and Kamlet filed a patent in which they reported that this filtration became much easier if they used modified conditions for the Sandmeyer reaction.¹¹ They found that dosing 5-AT in dilute nitric acid instead of dilute sulfuric acid as originally reported led to a dramatic reduction in the amount of time required for the isolation and washing of **1**. For this reason, as well as several other improvements,¹² this procedure is widely used today.



Scheme 1. Synthesis of DBX-1 from 5-aminotetrazole.

Complex **1** is a sensitive explosive when dry, and manipulating this material presents hazards to operators, especially as reaction scale increases. A differential scanning calorimetry (DSC) thermogram of this compound is presented in Figure 1. In a second step, **1** is manually

removed from the filter and charged to a reactor containing water. The resulting slurry is treated with aqueous sodium hydroxide, leading to the precipitation of copper(II) oxide, which is removed by filtration, leaving a solution of sodium 5-nitrotetrazolate (NaNT). The resulting solutions of NaNT typically contain a significant amount of residual 5-AT as an impurity (ca. 5% by weight of total dissolved species). To purify this material for conversion to transition metal 5-NT complexes, NaNT is typically isolated as its dihydrate, which becomes extremely sensitive if it is allowed to convert to the anhydrous form in dry air.^{10,11} This purification adds another operation to the procedure, adding cost and complexity to the process, and further increasing operator exposure to sensitive energetic solids.

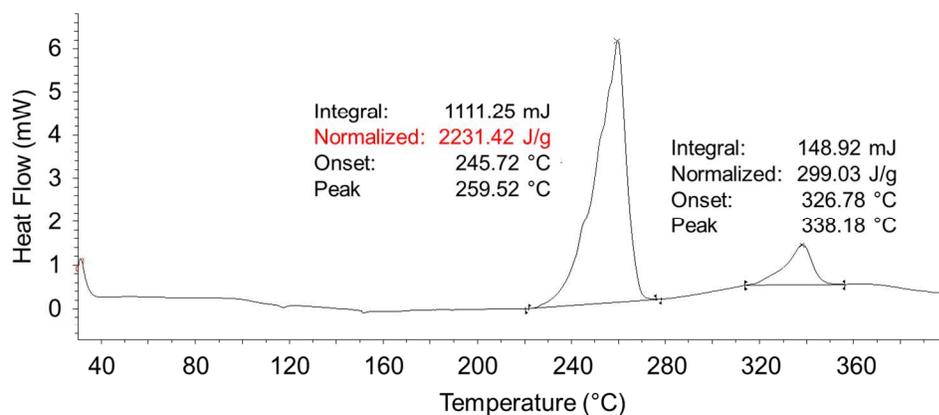


Figure 1. DSC thermogram for crude **1** (0.498 mg sample) measured in a high pressure gold pan at a scan rate of 5 °C/min.

To convert NaNT to DBX-1, an aqueous solution of NaNT is treated with copper(II) chloride and DBX-1 seed crystals, and sodium ascorbate is dosed slowly to the reaction mixture, reducing copper(II) to copper(I). As sodium ascorbate is dosed, a non-crystalline solid immediately precipitates. After an induction period of variable length, these solids convert into fine, red crystals of DBX-1. Irreproducibility has been a major challenge in synthesizing DBX-1:

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2
3 some reactions never convert to crystalline DBX-1. The amount of seed used, the dosing rate of
4 the reducing agent and the purity of the NaNT have been identified as important factors for
5 predicting whether a reaction will be successful. In a recent collaborative publication, we
6 studied the influence of impurities in NaNT on the reaction to form DBX-1 and developed a
7 purification protocol that could produce NaNT in sufficiently high quality to consistently
8 produce DBX-1.¹³

9
10 After we completed that work, we focused our efforts on further streamlining this
11 process, both to eliminate the hazardous step that requires the operator to transfer **1** off of a filter,
12 and also to eliminate purification steps for NaNT. In this article, we address both of those issues.
13 We demonstrate a synthesis of NaNT that produces NaNT that can be converted to DBX-1
14 without purification. In addition to the improved purity of the NaNT that this process affords, we
15 were able to improve the safety of the process by using a reactor with an internal filter. Using
16 this piece of equipment, **1** can be filtered and washed without removing it from the reactor,
17 eliminating handling of this intermediate. In the course of developing this process, we also
18 conducted a detailed analysis of the mass balance and the composition of the key intermediate **1**,
19 and those findings are presented in this article as well.

20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 **A. Role of the Solvent for 5-AT**

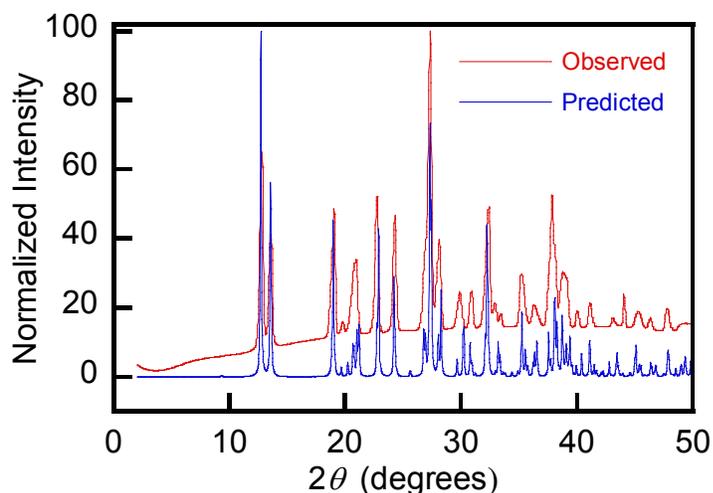
45
46 The nitro group in 5-NT is installed by a Sandmeyer reaction of 5-aminotetrazole,
47 accomplished by dosing a solution of 5-AT to a mixture containing sodium nitrite and a
48 copper(II) catalyst. This converts 5-AT to 5-NT, which precipitates from the reaction mixture as
49 complex **1**, a gelatinous solid. When performing this reaction, we observed that attempting to
50 dose solutions of certain concentrations of 5-AT in nitric acid resulted in the nitrate salt of 5-AT
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3 precipitating in the dosing lines. 5-AT nitrate is an impact-sensitive explosive reported to melt
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5 with violent decomposition at ca. 170 °C.^{14,15} In addition to the safety concerns in having this
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7 energetic material accumulate in the dosing lines, solid 5-AT nitrate being dosed to the copper
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9 sulfate/sodium nitrite solution could result in the precipitation of copper(II) complexes of 5-AT.
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11 If these complexes precipitate from solution at this point in the reaction, they would be isolated
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13 along with the copper(II) 5-NT complex **1**. As **1** is converted to the NaNT, the copper(II) 5-AT
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15 complexes would be converted back to free 5-AT and remain in solution as an impurity, making
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17 additional purification steps necessary before the NaNT could be used to produce DBX-1.
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22 To design a safer process and remove this potential source of 5-AT contamination, we
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24 performed a detailed study of the solubility of 5-AT in nitric acid. We also examined the
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26 solubility of 5-AT in sulfuric acid, as had been reported previously.¹⁰ We considered molar
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28 ratios of 1.0 and 2.0 equivalents of acid with respect to 5-AT, and varied the amount of water
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30 present as well. We found that 5-AT is at least twice as soluble in aqueous sulfuric acid as it is in
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32 aqueous nitric acid (details presented in the Supporting Information). The improved solubility of
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34 5-AT in sulfuric acid combined with eliminating the energetic 5-AT nitrate solids present in the
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36 dosing lines made sulfuric acid a very attractive choice.
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41 Given these data, we tested whether the improved solubility of 5-AT in sulfuric acid
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43 would translate to a process to synthesize higher purity NaNT. One concern we had with this
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45 modification is that the filtration of **1** prepared in this fashion is very tedious.¹¹ To speed up
46
47 filtering and washing steps, we found diatomaceous earth to be effective as a filtration aid, thus
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49 addressing the challenging physical properties of **1**. We were pleased to find that this procedure
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51 led to the production of **1** that could be converted to NaNT solutions that had levels of 5-AT that
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53 were typically below our limits of detection by HPLC.¹⁶ We were able to convert these solutions
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3 directly to DBX-1 without any additional purification steps. To confirm that the material
4 prepared by our method is DBX-1, we compared a powder X-ray diffraction (PXRD) data set of
5 our product with a powder pattern predicted for the reported solid state structure of DBX-1.⁶ We
6 found excellent agreement between the predicted and observed PXRD pattern (Figure 2),
7 providing conclusive evidence that the product of these reactions is DBX-1. To the best of our
8 knowledge, this is the only reported method for preparing DBX-1 from unpurified NaNT. This
9 modification to the process will allow for lower cost and more consistent production of DBX-1.
10 This protocol may also be useful for the production of mercuric 5-NT and other materials that
11 require NaNT free of impurities.
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44 **Figure 2.** Comparison of observed powder X-ray diffraction data for DBX-1 produced in this
45 work with the predicted powder pattern for DBX-1 based on the crystal structure published in
46 Ref. 6 (FWHM = 0.1°). The peak at ca. 45° in the observed pattern is due to the aluminum
47 sample holder.
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B. Full Characterization of the Process to NaNT

While using sulfuric acid as the solvent for 5-AT led to improved NaNT purity and process safety, we were still concerned by the fact that there were several aspects of the process that were not well understood. The largest of the issues that we hoped to resolve concerned the key copper(II) 5-NT complex **1**. This material has long been postulated to have the formula $\text{Cu}(\text{5-NT})_2(\text{H-NT})(\text{H}_2\text{O})_4$,¹¹ but its structure had never been rigorously established. Additionally, there were some major questions surrounding the mass balance. For one, the yield of NaNT is typically approximately 80% based on 5-AT, but it was not clear whether the yield loss was incurred in conversion of 5-AT to **1**, or from **1** to NaNT. In addition, the yield of NaNT was frequently greater than 100% based on NaOH dosed to **1**, indicating that our understanding of the composition of **1** was incomplete. These issues made it clear to us that a complete analysis of **1** would be necessary to further improve the process.

To address these ambiguities, we fully characterized the isolated copper(II) complex of 5-NT (**1**) and the NaNT solution. We began with a single reaction to produce enough of the copper(II) complex of 5-NT to characterize and to support the remainder of our studies. This ensured that our data were consistent throughout. To characterize **1** isolated from the Sandmeyer reaction of 5-AT, we used a wide array of analytical methods (see the Experimental section below). The yield of 5-NT from 5-AT (the limiting reagent) was 88%.¹⁷ The results of our analyses are presented in Table 1.

Table 1. Analysis of **1**

Component	Method ^a	Content (wt. %)	Content (molar ratio)
Copper	UV/vis	14	1
5-NT ^b	HPLC	63	2.5
Water ^c	TGA	13	3.3
Sodium	IC	4	0.8
Sulfate	IC	< 1	-
Nitrite	IC	< 1	-
Total		94	-

^aDetails of these methods are described below in the experimental section. ^bContent of 5-NT expressed as the acid form. ^cLoss of weight on heating by TGA from ca. 75–130 °C.

Finding that copper, 5-NT, and water only accounted for 90% of the composition of **1** by mass, we tested for additional components that have not typically been invoked in the composition of this material. Considering the conditions of the Sandmeyer reaction, we wondered whether the material might contain sodium, sulfate, nitrite, or nitrate ions. To evaluate this, we analyzed the material with ion chromatography methods (both anion- and cation-exchange columns). While sulfate, nitrite, and nitrate were not present in detectable quantities, we found a significant quantity of sodium ions in the material (4% by weight).

To the best of our knowledge, the presence of sodium in **1** has not been reported in the literature. The implications of this observation are significant for the following step in the sequence, as **1** is converted to an aqueous solution of sodium 5-nitrotetrazolate (NaNT). Past experience in our laboratories with that reaction is that dosing a full equivalent of sodium hydroxide with respect to 5-NT leads to a very high pH (>12) and a NaNT solution that does not produce DBX-1. The insight that sodium is present in the acid copper salt provides a rationale for dosing a substoichiometric amount of sodium hydroxide.

While this analysis shed light on the composition of **1**, we still felt that we had a less than complete understanding of this material. Therefore, in a separate study, a crystal of **1** was

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3 prepared by recrystallization and the solid state structure was solved using single crystal X-ray
4 diffraction data.¹⁸ The structure is presented in Figure 3. In this structure, the copper centers are
5
6 arranged in a 1D coordination polymer (i.e. infinite wires), with three 5-NT ligands bridging
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8 between each copper(II) center. Therefore, each copper(II) center is bound to six 5-NT ligands,
9
10 each 5-NT ligand is bound to two copper(II) centers, and each repeating unit has a charge of -1 .
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12 In the channels between these wires are a cluster of water molecules, as well as a counteranion
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14 to the polymer. In the solid state structure shown in Figure 3, that counteranion is a hydronium
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16 ion.
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22 The formula of **1** determined from the solid state structure is $\text{Cu}(\text{5-NT})_3(\text{H}_2\text{O})_3(\text{H}_3\text{O})$. This is
23
24 very similar to the originally stated composition, with the only significant difference being the
25
26 location of the acidic proton: in the structure shown in Figure 3, the acidic proton resides with a
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28 hydronium ion, whereas in the originally reported structure, one of the 5-NT units was in its
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30 protonated state.¹⁰ We note that this solid state structure does not provide a location for the
31
32 sodium ions identified above. In principle, the sodium ions could be counter-ions to the anionic
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34 repeat unit, or they could belong to a minor component of the material. In either case, the precise
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36 amount of sodium in isolated **1** may depend strongly on the exact conditions used for its
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38 synthesis and isolation.
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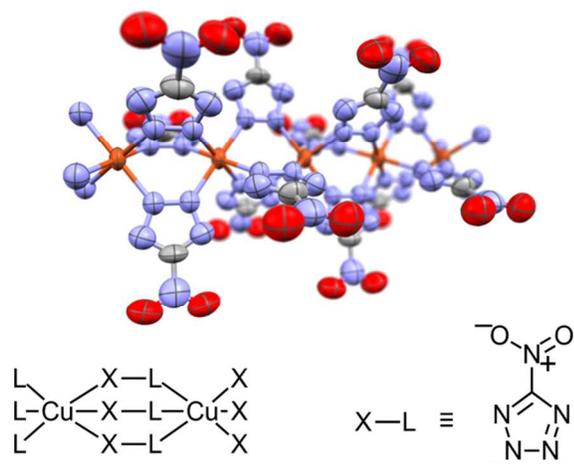


Figure 3. Solid state structure of crystal isolated by recrystallization of **1** from methanol. Color code: grey = carbon, blue = nitrogen, red = oxygen, and orange = copper

To establish that the material whose solid state structure is described above is the same material found in samples of **1** isolated from the Sandmeyer reaction, we collected a PXRD data set for crude **1**. We compared this to a PXRD dataset predicted for the crystal structure depicted in Figure 3. These two datasets are presented in Figure 4. The excellent degree of agreement is strong evidence for the solid state structure shown in Figure 3 being representative of **1** isolated en route to DBX-1.

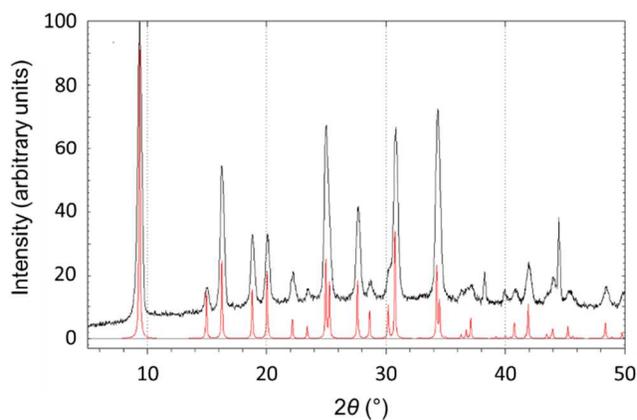


Figure 4. Comparison of PXRD patterns experimentally determined for **1** (black) and calculated for the structure in Figure 3 (red). Peaks at $2\theta = 38^\circ$ and 45° are due to the aluminum sample holder used for our analysis.

To complete our analysis of **1**, we converted a sample of this material to a NaNT solution. After suspending **1** in water and warming the mixture to 50°C , we slowly dosed a 4.82 N solution of sodium hydroxide. As we dosed this solution in small portions, the pH would rise rapidly before dropping to a lower value (Figure 5). As the dose progressed, the time required for the pH to reach a steady level increased, with the last portions of the pH correction taking hours to reach a stable value. At pH 10, we stopped our dose with 0.75 equiv NaOH dosed with respect to 5-NT present in **1**. Filtration of this mixture through a pad of Celite led to the removal of insoluble copper(II) oxide and the isolation of NaNT solution. We analyzed this solution along with two additional rinses of the filter cake.

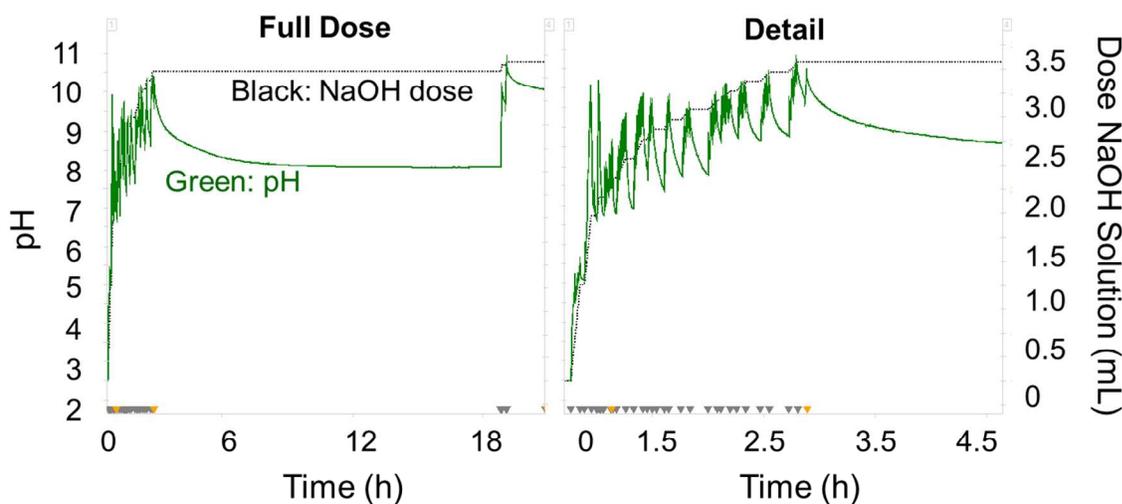


Figure 5. Online measurement of pH while dosing 4.8 N NaOH into a slurry of **1**.

The 5-AT concentration of this solution was 0.04% (w/w), an order of magnitude less than the 0.33% (w/w) concentration in solutions of purified NaNT used for DBX-1 synthesis in our

previous publication.¹³ The analysis of sodium and 5-NT levels in these solutions is presented in Table 2. Between the liquors and the two rinses of the filter cake, we were able to account for all of the 5-NT in **1** based on the analysis presented above. We note that the amount of sodium present in the NaNT solution cannot be explained by the sodium added in the form of sodium hydroxide – there is 51% more sodium present than would be expected based on the amount of NaOH dosed. If we take the sodium content of **1** into account, we are able to explain the origin of sodium in the NaNT solution (106% yield observed). This further emphasizes that understanding the sodium content of **1** is critical to understanding the conversion of **1** to NaNT. This analysis also demonstrates that while conversion of **1** to NaNT occurs in quantitative yield, some NaNT remains on the filter and must be rinsed out of the filter cake. Optimization of the filtration to diminish the amount of solution held up in the filter could provide a modest yield improvement.

Table 2. Analysis of NaNT solution.

Sample	5-NT mg/g	Na ⁺ mg/g	5-NT Yield ^a w.r.t. 1	Na ⁺ Yield ^b w.r.t. NaOH	Na ⁺ Yield ^b w.r.t. NaOH + 1
Liquors	58.7	8.79	88%	131%	92%
Rinse 1	15.1	2.29	13%	20%	14%
Rinse 2	0.3	0.06	0%	0%	0%
Total			101%	151%	106%

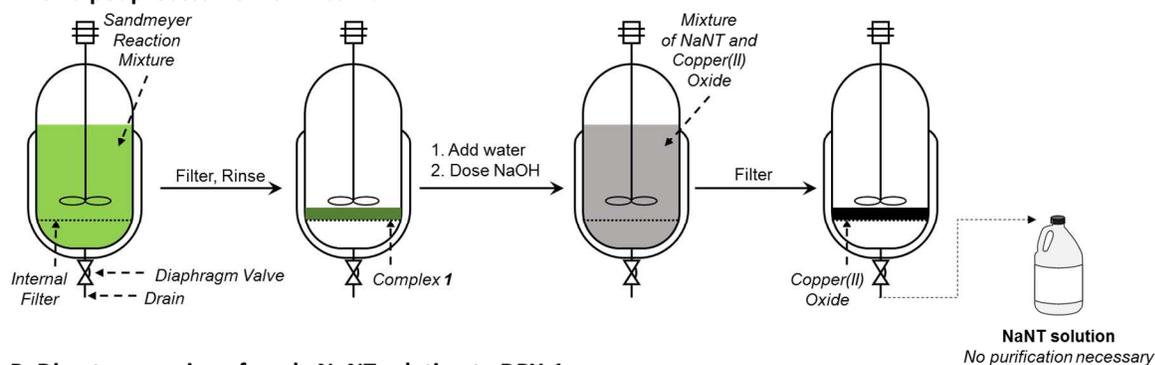
^aDetermined by HPLC. ^bDetermined by IC.

C. Development of a Lean Process to DBX-1

As discussed in the Introduction, two major limitations of the current synthesis of DBX-1 are that the explosive intermediate **1** must be isolated, and the fact that the NaNT must be purified before it can be converted to DBX-1. Earlier in this article, we demonstrated that the use of sulfuric acid solutions to dissolve 5-AT in place of nitric acid facilitates the synthesis of NaNT that does not require purification, but we still isolated intermediate **1** in that procedure. That material is a sensitive explosive when dry, and transferring it from the filter into a reactor places

the operator at risk and requires careful procedures to remove trace materials from the filter to prevent them from drying there. To diminish the hazards associated with solid **1**, we envisaged using a reactor with an internal filter that would enable us to isolate **1**, perform washes of that material, and convert it to NaNT, all without removing **1** from the reactor. This NaNT solution could be stored safely, or used directly in a second reactor to prepare DBX-1. A conceptual sketch of this process is presented in Figure 6.

A. One-pot process from 5-AT to NaNT



B. Direct conversion of crude NaNT solution to DBX-1

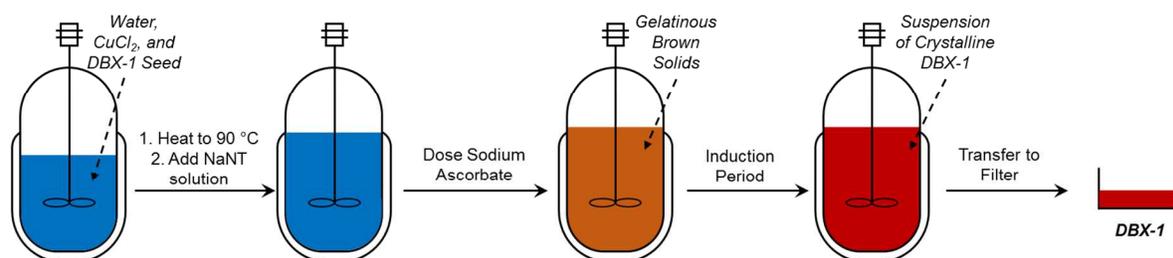


Figure 6. Lean process to DBX-1. A. Process to NaNT utilizing reactor with internal filter for synthesis of NaNT without manual manipulation of **1**. B. Process for converting crude NaNT solution to DBX-1 without prior purification.

To test this proposal, we performed a small scale reaction in a 100-mL reactor and removed the reaction liquors and rinses of **1** manually using a pipette after allowing the solids to settle. We found that this led to NaNT of high purity, and this NaNT could be converted to DBX-1

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3 without further purification. Based on those results, we tested this approach at the 600-mL scale
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5 using a commercially available filter reactor. We charged diatomaceous earth to the reactor prior
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7 to filtering **1** to assist in filtering that material, and left the diatomaceous earth in place to assist
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9 the filtration of copper oxides from the NaNT solution. The sensitive intermediate **1** remained
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11 wet at all times and was never handled by the operator. Using this procedure, we were able to
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13 isolate highly pure NaNT solutions in 56% yield from 5-AT. We were then able to use this
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15 solution directly to produce DBX-1.
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20 To improve the reliability of the reaction from NaNT to DBX-1, we have made several
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22 modifications to the original procedure first disclosed by researchers at Pacific Scientific
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24 Energetic Materials Corporation.⁶ Some of these modifications were presented in our previous
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26 publication on DBX-1.¹³ The most significant modification is that we seed our reactions with
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28 authentic DBX-1 before dosing sodium ascorbate. Typical loadings of seed range from 1% to
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30 25% by weight relative to the theoretical yield of DBX-1. This dramatically reduces the length of
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32 the induction period, and reduces the likelihood of a batch of NaNT not converting to DBX-1.
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34 This is especially important on large scale, because if a reaction does not convert, it cannot be
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36 salvaged. A second modification is that we dose our sodium ascorbate solution in two portions.
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38 The first portion, 15% of the total, is dosed slowly (0.1 mL/min of a 1 M solution on the lab
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40 scale). After this dose, the reaction mixture is stirred until the gelatinous brown material
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42 transforms to DBX-1. This effectively increases the amount of seed for the second dose of the
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44 remaining 85% of the sodium ascorbate, which can then be dosed at a faster rate (0.5 mL/min).
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46 The combination of these two modifications allows us to achieve a high level of reproducibility
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48 in synthesizing DBX-1.
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3 The novel processing techniques discussed above have resulted in an efficient method to
4 produce high quality DBX-1 with improved operator safety. Future work will focus eliminating
5 “dead space” below the filter plate of the NaNT reactor, as this space can allow solids to collect
6 during the reactions. The process will also be improved by enabling remote operation.
7
8 Eliminating the necessity of an operator interacting directly with the reactor for manual
9 operations and additions increases the overall safety of the process and is an absolute
10 requirement for transition to manufacturing at larger scales. The development of this remotely-
11 operated manufacturing process is a focus of our current efforts.
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24 **Conclusion**

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26 The study presented above provides a strategy for producing the lead-free primary explosive
27 DBX-1 with significant safety and operational improvements. A summary of the most significant
28 advances is presented in Table 3. The cornerstone of our work was a detailed analysis of the
29 little-understood process to produce the intermediate NaNT. This analysis led to the development
30 of an improved process for the production of NaNT that does not require purification before
31 being converted to DBX-1. This process marks a significant advance over previously reported
32 procedures that rely on isolation of the explosive intermediate **1** and manual charging of this
33 material to a reactor, as well as purification of the NaNT prior to conversion to DBX-1. Our
34 study of the improved process led to the a detailed analysis of the mass balance on this process
35 and confirmation that **1** is the same composition as the recently reported solid state structure of
36 $\text{Cu}(5\text{-NT})_3(\text{H}_2\text{O})_3(\text{H}_3\text{O})$.
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Table 3. Comparison of this work with previously disclosed processes for preparing DBX-1.

	Previous reports	This work
Precipitation of explosive 5-AT nitrate in dosing lines	Yes	No
Operator handling of 1	Yes	No
Purification of NaNT required	Yes	No

This work provides a foundation for the safe and reliable production of DBX-1 to support efforts in the energetic materials community to replace LA with more environmentally friendly and chemically inert DBX-1 in detonators. Future work in our laboratories will focus on gaining understanding of the chemical processes that take place in the conversion of NaNT to DBX-1, and the transition of this process to the manufacturing scale.

Experimental Section

WARNING! The materials prepared and analyzed in these procedures are explosives that are sensitive to impact, friction, and electrostatic discharge. Safely synthesizing and handling these materials requires specialized training and equipment.

General information. Reagents were used as received. All water used in these procedures was deionized water. pH probes were calibrated immediately prior to use and were used with temperature compensation based on the reaction temperature. A Mettler Toledo 822e Differential Scanning Calorimeter was used in this study after calibration with Indium (6-7 mg, 99.999% pure, $T_{\text{onset}} = 156.6^{\circ}\text{C}$) and Zinc (2-3 mg, 99.999% pure, $T_{\text{onset}} = 419.6^{\circ}\text{C}$). Samples (0.1 mg to 0.3 mg) were prepared in high pressure gold pans and scanned at $5^{\circ}\text{C}/\text{min}$. from 30°C to 400°C . Background curves were collected using the same pan configuration and method with

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2
3 a nitrogen purge for all analysis. Onset temperatures for endothermic and exothermic transitions
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5 were determined by employing the baseline tangent peak tangent method and when appropriate a
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7 linear baseline was constructed to integrate the area under the curve to determine the heat of
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9 decomposition. Powder x-ray diffraction data were collected on a Rigaku MiniFlex600
10
11 diffractometer equipped with a copper source at 30 kV, and 15 mA typically scanned over a
12
13 range of 2-40 degrees (2-Theta). Samples were prepared on an aluminum holder with a 0.2mm
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15 cavity and rotated continuously throughout data collection. For the analytical methods described
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17 below, sample concentrations were determined using the calibration curve method. A multi-level
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19 calibration curve was generated using standard solutions and test sample concentration was
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21 determined by interpolation on the curve. In some cases, the concentrations of minor components
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23 were estimated by extrapolation from the low level of the calibration curve. Details and HPLC
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25 data are provided in the Supporting Information.
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31 **Method for determining 5-NT content.** 5-nitrotetrazole content was determined using a
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33 calibrated HPLC method. Crystalline NaNT dihydrate was prepared as described previously,¹¹
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35 and was found to have a potency of 98% after determination of water and sodium content. This
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37 material was used as a reference standard for 5-NT concentration determinations. Column:
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39 Thermo Scientific Hypercarb, 4.6 mm × 100 mm, 5 μm (Part Number 35005-104630). Mobile
40
41 Phase: MP A = 0.5% perchloric acid, MP B = Acetonitrile. Gradient: 95% MP A / 5% MP B to
42
43 85% MP A /15% MP B from 0 to 9 minutes. Flow Rate: 1 mL/min. Temperature: 40 °C.
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45 Injection Volume: 5 μL. Detection Wavelength: 215 nm. NaNT solution sample preparation:
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47 120–150 mg sample diluted to 10 mL with water. Sample preparation for 1: Dissolve 25 mg
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49 sample in 4 mL ammonium hydroxide (28% solution), then dilute to 100 mL with water.
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3 **Method for determining copper(II) content in complex 1.** We developed a UV/Vis
4 absorbance method for quantifying copper(II) content based on the fact that 4-(2-
5 pyridylazo)resorcinol (PAR) forms a complex with copper(II) that absorbs light at a wavelength
6 of approximately 500 nm.¹⁹ The PAR reagent solution was prepared by weighing approximately
7 PAR (34 mg), sodium bicarbonate (0.95 g), and aqueous ammonium hydroxide (28%, 2.3 g) into
8 a 100 mL volumetric flask. Those materials were dissolved and the solution diluted to 100 mL
9 with water. A stock solution was prepared for analysis by weighing complex **1** (ca. 25 mg) into a
10 100 mL volumetric flask. Aqueous ammonium hydroxide (28%, 5 mL) was added and swirled to
11 totally dissolve the sample and the resulting solution was diluted to 100 mL with water. In a 100
12 mL volumetric flask, a 1 mL portion of this sample stock solution was mixed with 4 mL of the
13 PAR reagent solution, and the resulting solution was diluted to 100 mL with water. The
14 absorbance of this solution at 500 nm was recorded and compared with a standard material
15 (copper(II) sulfate pentahydrate) and a blank prepared identically to the sample stock solution,
16 but without **1**.
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36 **Method for determining sodium content.** Sodium levels were determined using a calibrated
37 ion chromatography method. Column: Waters IC-Pak Cation M/D, 3.9 mm × 150 mm, 5 μm
38 (Part No. WAT036570). Mobile Phase: 0.1 mM EDTA with 3 mM nitric acid in water. Flow
39 Rate: 1 mL/min. Temperature: 30 °C. Injection Volume: 50 μL. Detection: conductivity. Sample
40 preparation for **1**: 20 mg sample + 0.5 mL EDTA stock solution, to 25 mL with water. EDTA
41 stock solution is a 1 mg/mL solution of disodium EDTA in water. This was compared to a blank:
42 0.5 mL EDTA stock solution diluted to 25 mL with water. Sample preparation for analysis of
43 NaNT solutions: 100–150 mg diluted to 50 mL with water.
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3 **Method for determining anion content.** Sulfate, nitrate, and nitrite levels were determined
4 using a calibrated ion chromatography method. Column: Waters IC-Pak Anion HC, 4.6 mm ×
5 150 mm (Part Number WAT026770). Mobile Phase: 86% Gluconate buffer + 12% Acetonitrile
6 + 2% Butanol. Flow Rate: 2 mL/min. Temperature: 30 °C. Injection Volume: 50 µL. Detection:
7 conductivity. Sample preparation was the same as for the sodium method above.
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10 **Sodium 5-Nitrotetrazolate (NaN₂T).** A 600-mL jacketed filter reactor was fitted with a glass
11 radial flat-bladed turbine, temperature probe, pH probe, and a 10–20 µm filter disc. Reagent
12 doses with specified dosing rates were performed by using a peristaltic pump to dose reagent
13 solutions from a bottle on a balance. The pumping rate was controlled to achieve the desired
14 gravimetric dosing rate. A solution containing water (117 g), copper(II) sulfate pentahydrate
15 (21.4 g, 0.0855 mol), and sodium nitrite (53.6 g, 0.776 mol) was charged to the reactor and the
16 temperature of the reaction mixture was controlled to 10 °C. A solution containing water (272 g),
17 98% sulfuric acid (19.5 g, 0.195 mol), 5-aminotetrazole (16.5 g, 0.194 mol), and copper(II)
18 sulfate pentahydrate (0.775 g, 0.0031 mol) was dosed to the reactor at a rate of 2.1 g/min,
19 keeping the reaction temperature below 14 °C. A solution containing water (20.5 g) and 98%
20 sulfuric acid (21.3 g, 0.213 mol) was dosed to the reactor at a rate of 1.3–2.6 g/min, keeping the
21 reaction temperature below 15 °C. The reaction mixture was stirred for 1 hour. Diatomaceous
22 earth (19.3 g) was added in one portion and stirred into the reaction mixture before stirring was
23 stopped and the reactor drain was connected to a side-arm vacuum flask. *Warning! The solids
24 collected on the filter are extremely sensitive energetic materials when dry. Do not allow the
25 solids to dry. If filter breakthrough is observed and solids pass around the filter, closing the
26 drain valve could compress these materials and result in energetic initiation. This could lead to
27 equipment damage and operator injury. Do not close the drain valve until the washes are*
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3 *complete*. This flask was placed under vacuum with small diaphragm vacuum pump, draining the
4 reaction liquors into the flask. A solution containing water (219 g) and 98% sulfuric acid (24.9 g)
5 was added to the reactor in one portion. The mixture was stirred for five minutes, then stirring
6 was stopped and the contents were drained by the same method as above. Water (228 g) was
7 added to the reactor in one portion and the mixture was stirred briefly, then stirring was stopped
8 and the contents were drained by the same method as above. The final water wash was repeated
9 two additional times, at which point the filtrate had a pH of 1.3. Water (282 g) was added to the
10 reactor and stirring was resumed to achieve a slurry. The reaction temperature was increased to
11 50 °C. A 50% (w/w) aqueous solution of sodium hydroxide was dosed in portions to the reaction
12 mixture until the reaction mixture reached pH 9.1 (9.08 g added, 0.114 mol). As the sodium
13 hydroxide is dosed, the green solids suspended in the reaction are replaced by black solids. After
14 the dose of sodium hydroxide was complete, the reaction temperature was increased to 70 °C.
15 The mixture was stirred at this temperature for 1 hour, then stirring was stopped and the liquors
16 were drained by the same procedure as above. The first portion of filtrate (36.4 g) is
17 contaminated with black solids due to a small amount of the material being formed below the
18 filter plate. The second portion (292.3 g) was free of solids. This solution was found to contain 5-
19 NT (6.39% w/w as NaNT dihydrate), nitrite (0.072% w/w), nitrate (0.070% w/w), and sulfate
20 (0.079% w/w). 5-AT was not detected. The solution that was free of solids provided the
21 equivalent of 18.7 g of NaNT dihydrate (0.108 mol, 55.7% yield).

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48 **Copper(I) 5-Nitrotetrazolate (DBX-1)**. A 100-mL reactor was fitted with a glass pitched-blade
49 impeller, internal temperature probe, and additional probes to monitor particle size and visualize
50 particle morphology (Mettler Toledo FBRM[®] and PVM[®]). The reactor was charged with DBX-1
51 seed (22.0 mg) that was suspended in water (35.0 g) and stirring was initiated. The reactor was
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3 charged with an aqueous solution of copper(II) chloride (1 M, 12.2 mL, 12.2 mmol, 1.05 equiv.).
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5 The reaction temperature was increased to 90 °C over 30 minutes. The reactor was then charged
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7 with an aqueous solution of NaNT (27.0 g, 7.4% w/w 5-NT, 11.6 mmol, 1.00 equiv). This NaNT
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9 solution was prepared by blending lots prepared using the 600 mL procedure described above.
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11 The solution was not purified prior to use. After the NaNT solution has been added, a syringe
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13 pump was set up to dose a 1.0 M aqueous solution of sodium ascorbate (1 M, 0.95 mL, 0.082
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15 equiv.) at a rate of 0.1 mL/min. This caused the clear, blue solution to turn into a turbid, brown
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17 suspension of gelatinous solids. After 42 minutes, the solids rapidly transformed into dark red
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19 crystalline solids suspended in a clear liquors. At this point, additional 1.0 M aqueous sodium
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21 ascorbate was dosed to the reaction mixture (5.36 mL, 0.46 equiv.) at a rate of 0.5 mL/min. After
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23 this dose, the reaction mixture consisted of dark red crystalline solids suspended in clear liquors.
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25 The stirring was stopped, allowing the solids to settle to the bottom of the reactor. The liquors
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27 were carefully drawn out using a peristaltic pump. Water (25 mL) was added to the reactor, and
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29 the mixture was stirred until the mixture reaches at least 85 °C. At that point, the stirring is
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31 stopped, and the solids were allowed to settle. The liquors were removed using a peristaltic
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33 pump. This rinse is repeated one additional time. A final portion of water (25 mL) was added to
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35 the solids and the mixture was stirred until the reaction temperature reaches at least 85 °C.
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37 *WARNING! DBX-1 is a sensitive primary explosive. Dry solids pose a very high risk of energetic*
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39 *initiation. Take care not to allow any spilled solids to dry.* At this point, the reactor lid and
40
41 probes are removed, and the reactor contents were transferred to a Büchner funnel fitted with a
42
43 filter paper disc. The isolated solids were rinsed twice with 2-propanol and transferred to a
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45 conductive container for storage. After drying, the container had a net weight of 1.7 g DBX-1
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47 (85% yield). The PXRD pattern matches the predicted pattern for DBX-1 with no additional
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3 peaks other than those due to the sample holder (see Figure 2), $T_{\text{onset}} = 302.8 \text{ }^{\circ}\text{C}$ (5 $^{\circ}\text{C}/\text{min}$, 0.315
4 mg sample) by DSC.
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10 ASSOCIATED CONTENT

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13 **Supporting Information.** Solubility data for 5-AT, data from HPLC, IC, and TGA analyses, as
14 well as details of the experimental setup for the improved NaNT process are provided in the
15 Supporting Information. This material is available free of charge via the Internet at
16 <http://pubs.acs.org>.
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27 AUTHOR INFORMATION

28 Author Contributions

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32 §These authors contributed equally.
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44 quite stable under air, and can be stored for extended periods of time under ambient conditions
45 without appreciable degradation. We are unaware of a specific explanation for the stability of
46 DBX-1, other than to say that its structure in the crystalline form may offer protection and
47 improve stability. These copper centers can be oxidized under more forcing conditions, though:
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32 12 Another important advance was the elimination of the “microdetonations” that accompanied
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34 dosing 5-AT using the von Herz procedure. Gilligan and Kamlet write that these were “not
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36 harmful in themselves, [but] were psychologically disturbing and did on occasion break
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38 glassware.” There were due to gaseous nitrous acid reacting with 5-AT to generate the
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40 diazonium species before the solution had mixed with the solution containing the catalyst.
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42 Without a catalyst present, this highly unstable material would decompose rapidly. Gilligan and
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44 Kamlet solved this problem by adding a small quantity of a copper(II) salt to the solution of 5-
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46 AT. This would catalyze the reaction of the diazonium species before it could accumulate and
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detonate.

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21 16 Our estimated limit of detection for the assay is 0.001 mg/mL 5-AT. In samples prepared
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23 for simultaneous 5-AT and 5-NT analysis the sample must be diluted to bring the 5-NT
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25 concentration within the calibrated range. After dilution, the limit of detection for 5-AT is
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27 approximately 0.1 mg/mL.

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29 17 This yield is based on the potency-corrected amount of 5-AT used. The 5-AT was 98.5%
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31 potent.

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