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Preparation and Crystal Structures of Two Salts with the 5-Nitrotetrazolate Anion

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ABSTRACT: *Tetraphenylphosphonium 5-nitrotetrazolate (**2**) was prepared by metathesis of sodium 5-nitrotetrazolate dihydrate (**1**; NaNT) with tetraphenylphosphonium chloride in acetone. The new compound was fully characterized by vibrational (IR, Raman) and NMR (^{1}H, ^{13}C, and ^{14}N) spectroscopies, elemental analysis, and mass spectrometry. Attempted synthesis of 2-methyl-5-nitrotetrazole (2-MeNT) by methylation of* **1** *with dimethylsulfate at reflux from acetonitrile failed, and crystals of an explosive compound with the formula $(NaNT)_2(H_2O)_2CH_3CN$ (**3**), NT = 5-nitrotetrazolate, formed. X-ray diffraction techniques were used to determine the crystal structure of* **2** *and* **3**. *Compound* **2** *crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell and unit cell parameters $a = 7.7413(4)$ Å, $b = 13.624(1)$ Å, $c = 21.252(1)$ Å, and $V = 2241.5(2)$ Å^3, whereas* **3** *crystallizes in the orthorhombic space group Ama2 with four formula unit in the unit cell and unit cell parameters $a = 14.805(6)$ Å, $b = 9.908(4)$ Å, $c = 8.940(3)$ Å, and $V = 1311.4(1)$ Å^3.* © 2009 Wiley Periodicals, Inc. Heteroatom Chem 20:35–44, 2009; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20509

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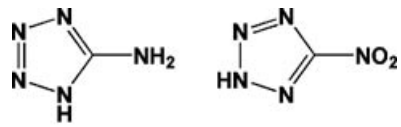
INTRODUCTION

The synthesis of nitrogen-rich compounds for use as highly energetic materials is the goal of our research group [1–4]. 5-Amino-1*H*-tetrazole (**A**) and 5-nitro-2*H*-tetrazole (**B**) are nitrogen-rich energetic compounds, which are readily deprotonated by bases [5,6]. Nitrogen-rich salts of **B** with easily protonated nitrogen bases [7] have shown interesting properties in terms of low sensitivities and high performances. We recently synthesized metal salts of **A**, which are prospective candidates for use in new environmentally friendly pyrotechnic compositions [5] and metal salts of **B**, which show an increased sensitivity to shock and friction [6]. The presence of crystal water in the solid-state structure of metal salts of **B** increases the distances between the metal center and the anion, and the sensitivity of the compounds toward classical stimuli is markedly reduced.

To investigate 5-nitrotetrazole moieties, which do not interact in the solid state we synthesized the tetraphenylphosphonium salt of **B** (**2**). In addition, synthesis of neutral 2-methyl-5-nitrotetrazole (2-MeNT) was attempted and bis-(sodium 5-nitrotetrazolate) dihydrate acetonitrile adduct (**3**) formed instead. Here, we would like to report on the synthesis and characterization of **2** and **3** as well as their crystal structures. To our knowledge, together

with our reports [6,7] and that of the nickel salt [8], these are the only papers where the structure of the anion of **B** has been determined by X-ray analysis.



A B

EXPERIMENTAL SECTION

Materials and Methods

CAUTION: Tetrazoles are energetic materials. Sodium 5-nitrotetrazolate dihydrate (**1**) has low sensitivity against friction and electrostatic discharge; however upon loss of water and/or rapid heating, it becomes highly sensitive and explosive. Safety equipment such as leather gloves, face shield, earplugs, and use of Teflon spatulas are recommended. It is not recommended the synthesis and manipulation of compound **1** on scales greater than 200 mg.

All chemicals and solvents were used as supplied by Sigma-Aldrich Fine Chemicals Inc. (Munich, Germany) without any further purification. Sodium 5-nitrotetrazolate dihydrate (**1**) was synthesized according to the literature [9,10]. ^{1}H, ^{13}C, ^{14}N, and ^{31}P NMR spectra were recorded on a JEOL Eclipse 400 instrument in DMSO-d_6 at room temperature. The infrared (IR) spectrum of **2** was recorded on a Perkin–Elmer spectrum one FT-IR instrument [11] (vs = very strong, s = strong, m = medium, w = weak, and vw = very weak). A Perkin–Elmer spectrum 2000R NIR FT-Raman instrument equipped with a Nd: YAG laser (1064 nm) was used for the recording of the Raman spectra (intensity percentages are given in brackets). A Netsch simultaneous thermal analyzer STA 429 was used to perform the elemental analyses. A differential scanning calorimetry (Linseis DSC PT-10 instrument [12], calibrated with standard pure indium and zinc) was used to determine the melting point and decomposition temperature of **2** (2°C min^{-1}). Closed aluminum sample pans with a 1-μm hole in the top for gas release under a nitrogen flow of 20 mL min^{-1} were used.

*Tetraphenylphosphonium 5-Nitrotetrazolate (**2**)*

Tetraphenylphosphonium chloride (0.314 g, 0.84 mmol) was dissolved in 15 mL dry acetone under an stream of nitrogen before a solution of sodium 5-nitrotetrazolate dihydrate (0.145 g, 0.84 mmol) in 5 mL dry acetone was added under a stream of nitrogen. Immediate precipitation of sodium chloride was observed, and the reaction mixture was stirred for further 20 min at room temperature. The insoluble solid was filtered and discarded, and the acetone solution was left to slowly evaporate yielding a slightly yellow residue of the product, which could be purified by dissolving it in minimal acetone and letting ether to diffuse into it overnight. The crystals formed were suitable for X-ray analysis (301 mg, 79%).

Analytical Data of **2**. Raman $\tilde{\nu}$/cm^{-1} (rel. int.): 3149(4), 3146(5), 3068(45), 2958(3), 1586(49), 1576(20), 1527(12), 1441(6), 1403(100), 1307(4), 1187(11), 1166(13), 1109(13), 1099(22), 1040(37), 1029(24), 1014(50), 1002(69), 834(7), 726(4), 679(14), 617(8), 531(5), 287(9), 254(21), 205(12), 143(6); IR $\tilde{\nu}$/cm^{-1} (KBr, rel. int.): 3437(w), 3091(w), 3051(w), 3024(w), 2820(vw), 2691(vw), 2204(vw), 1991(vw), 1833(vw), 1700(vw), 1585(w), 1572(w), 1558(w), 1526(s), 1482(m), 1440(s), 1435(s), 1428(s), 1404(s), 1340(w), 1307(s), 1182(w), 1162(m), 1152(w), 1107(vs), 1038(w), 1020(w), 997(m), 853(vw), 835(s), 757(s), 723(s), 691(s), 678(m), 672(m), 614(w), 478(vs), 456(m); ^{1}H NMR (DMSO-d_6, 400.18 MHz, 25°C, TMS) δ/ppm: 7.98–7.94 (4H, m, *p*-H), 7.84–7.71 (16H, m, *o*−H/*m*-H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100.6 MHz, 25°C, TMS) δ/ppm: 165.2 (1C, s, C1), 135.3 (4C, d, $^{4}J_{C\text{-}P} = 2.7$ Hz, *p*-C), 134.5 (8C, d, $^{2}J_{C\text{-}P} = 10.8$ Hz, *o*-C), 130.4 (8C, d, $^{3}J_{C\text{-}P} = 12.7$ Hz, *m*-C), 117.7 (4C, d, $^{1}J_{C\text{-}P} = 89.2$ Hz, *i*-C); ^{31}P NMR (DMSO-d_6, 162.00 MHz, 25°C, 35% H_3PO_4) δ/ppm: +23.0 (P); ^{14}N NMR (DMSO-d_6, 28.92 MHz, 25°C, CH_3NO_2) δ/ppm: +21 (2N, $\nu_{1/2}$ ~420 Hz, N2/3), −21 (1N, $\nu_{1/2}$ ~80 Hz, -NO_2), −58 (2N, $\nu_{1/2}$ ~400 Hz, N1/4); $C_{25}H_{20}N_5O_2P$ (453.44 g mol^{-1}, calc/found): C 66.22/66.11, H 4.45/4.44, N 15.45/15.37; *m/z* (FAB^{+}, xenon, 6 keV, m-NBA matrix): 339.34 $[PPh_4]^{+}$; (FAB^{-}, xenon, 6 keV, m-NBA matrix): 114.0 $[NT]^{-}$, 228.8 $[H(NT)_2]^{-}$; DSC (2°C min^{-1}): 125.7°C (mp), ~188°C (dec); Sensitivity data: friction >360 N; shock >30 J; electrost disch insensitive.

*Bis(sodium 5-nitrotetrazolate) Dihydrate Acetonitrile Adduct (**3**)*

Sodium 5-nitrotetrazolate dihydrate (0.294 g, 1.70 mmol) was refluxed in 10 mL acetonitrile for 2 h after which time the heating was switched off, and the solvent was rotavaporated down at 60°C to ~4 mL. Immediate precipitation of the product was observed, and the yield was increased by putting the mother liquors in the fridge overnight. The solid was filtered and washed with ether, rendering 0.382 g of

a colorless solid. Some of the crystals precipitated in the fridge were measured by X-ray analysis, confirming the formation of **3**.

Analytical Data of **3**. Raman $\tilde{\nu}$/cm^{-1} (rel. int.): 3015(3), 2950(5), 1548(7), 1424(100), 1363(4), 1319(5), 1180(4), 1056(47), 1044(41), 921(2), 841(4), 774(2), 546(3), 459(2), 392(2), 248(2), 145(2); ^{1}H NMR (DMSO-d_6, 400.18 MHz, 25°C, TMS) δ/ppm: 4.57 (~4H, s, H_2O), 1.97 (3H, s, CH_3); ^{13}C{^{1}H} NMR (DMSO-d_6, 100.63 MHz, 25°C, TMS) δ/ppm: 165.2 (2C, C/C1), 118.2 (1C, CN), 1.4 (1C, CH_3); ^{14}N NMR (DMSO-d_6, 28.92 MHz, 25°C, CH_3NO_2) δ/ppm: +22 (2N, $\nu_{1/2}$ ~400 Hz, N2/4), -19 (1N, $\nu_{1/2}$ ~70 Hz, -NO_2), -60 (2N, $\nu_{1/2}$ ~370 Hz, N1/3); *m/z* (FAB$^-$, xenon, 6 keV, m-NBA matrix): 114.0 [NT]$^-$, 228.8 [H(NT)$_2$]$^-$; DSC (5°C min^{-1}): ~200 °C (dec), Sensitivity data: friction >360 N; shock >30 J; electrost disch insensitive.

X-ray Structure Determinations of **2** *and* **3**

Compounds **2** and **3** were characterized by X-ray structure determination (Table 1). Crystals were grown as described in the Preparation Section. The X-ray crystallographic data were collected on an Oxford Diffraction Xcalibur 3 diffractometer equipped with a CCD detector at a temperature of 200 K (**2**) and 100 K (**3**) and using the CrysAlis CCD software [13]. All data were collected using graphite-monochromated Mo *Kα* radiation. No absorption correction was applied to the data sets collected. The data reduction was performed with the CrysAlis RED software [14].

Structure Analysis and Refinement. The crystal structures of **2** and **3** were solved by direct methods using the corresponding programs available in the WinGX package [15–18], and the structures were finally checked using the program PLATON [19]. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were located from difference Fourier electron density maps and refined isotropically. A SCALE3 ABSPACK multiscan method was used for the absorption correction [20].

Further information on the crystal–structure determinations (excluding structure factors) has been deposited at the Cambridge Crystallographic Data Centre (CCDC) under numbers CCDC 673959 (**2**) and CCDC 673958 (**3**) and is available free of charge by request from the CCDC. A copy of the cif file for compounds **2** and **3** can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code_(1223)336–033. E-mail for inquiry: fileserv@ccdc.cam.ac.uk. E-mail for deposition: deposit-@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Tetraphenylphosphonium 5-nitrotetrazolate (**2**) was prepared in high yield and purity by a metathesis reaction between sodium 5-nitrotetrazolate dihydrate (**1**) [9,10] and tetraphenylphosphonium chloride in acetone according to Eq. (1). After filtering the precipitated sodium chloride the solvent was stripped, and crystals were grown by storage of a saturated solution of the compound in acetonitrile in the refrigerator. Attempted synthesis of highly energetic neutral 2-methyl-5-nitrotetrazole (2-MeNT) by boiling **1** with an excess dimethylsulfate in acetonitrile failed, and an adduct with the formula $(NaNT)_2(H_2O)_2CH_3CN$ (**3**) was formed together with unreacted **1**. The result was reproducible when this reaction was repeated without the presence of dimethylsulfate (Eq. (2)).

$$\underset{\mathbf{1}}{Na^+NT^-} + PPh_4^+Cl^- \xrightarrow[-NaCl]{Acetone} \underset{\mathbf{2}}{PPh_4^+(cation)NT^-} \quad (1)$$

$$\underset{\mathbf{1}}{Na^+NT^-} \xrightarrow[reflux]{CH_3CN} (NaNT)_2 \cdot \underset{\mathbf{3}}{2H_2O} \cdot CH_3CN. \quad (2)$$

Compounds **2** and **3** were characterized by vibrational spectroscopy. The shifts for the cation in **2** are well established, and thus a description is omitted. Much more interesting are the bands corresponding to the 5-nitrotetrazolate anion in **2** and **3** that could be assigned by comparison with the calculated shifts [7,21]: ~1530 [$\nu_{asymm}(NO_2)$], ~1400 [ν_{asymm}(N—C—N)], ~1380 [$\nu_{symm}(NO_2)$ + ν_{symm}(N—C—N), "in phase"], ~1300 [$\nu_{symm}(NO_2)$ + ν_{symm}(N—C—N), "out of phase"], ~1180 [ν_{asymm}(tetrazole)], ~1160 [ν_{symm}(Tetrazole) + $\nu_{symm}(NO_2)$, "in phase"], ~1020 [δ(N—C—N) + $\nu_{symm}(NO_2)$, "in phase"], ~1000 [ν(N—N) + δ_{symm}(tetrazole), "out of phase"], ~835 [$\delta(NO_2)$ + δ(N—C—N), "in of phase"], ~765 [$\gamma(NO_2)$ + γ(N—C—N), "out of phase"], ~720 [γ(tetrazole) "in phase"], ~670 [γ(tetrazole) "out of phase"], 522 [$\omega(NO_2)$ + ω(tetrazole), "out of phase"], ~455 [ν(C–N) + $\delta(NO_2)$], ~250 [$\omega(NO_2)$ + ω(tetrazole), "in phase"], and ~205 [γ(N—C—N)] cm^{-1}. The most significant fact in the Raman spectrum of **2** is that the asymmetric nitro-group stretching is shifted and split in two signals at 1586 and 1576 cm^{-1} and the symmetric nitro-group stretching is strongly shifted (~15 cm^{-1}). This is indicative of little interaction between the nitro-group and the cation as confirmed by the crystal structure of the compound (see X-Ray Structure Discussion). On the other hand, for compound **3** the nitro-group stretches are observed much closer to the calculated values, indicative of strong interaction by the nitro-group oxygen atoms

TABLE 1 Crystal Data and Refinement for Compounds **2** and **3**

	2	**3**
Chemical formula	$C_{25}H_{20}N_5O_2P$	$C_4H_7N_{11}O_6Na_2$
Molecular weight	453.43	351.19
Crystal size	0.3 × 0.15 × 0.1	0.15 × 0.15 × 0.05
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	*Ama2*
a (Å)	7.7413(4)	14.805(6)
b (Å)	13.624(1)	9.908(4)
c (Å)	21.252(1)	8.940(3)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V(Å^3)	2241.5(2)	1311.4(1)
Z	4	4
$\rho_{calc.}$ (g/cm^3)	1.342	1.778
μ (mm^{-1})	0.156	0.211
F(000)	944	712
θ range (°)	3.84–28.99	4.11–29.97
Temperature (K)	200(2)	100(2)
Index range	$-10 \le h \le 10$ $-18 \le k \le 18$ $-28 \le l \le 28$	$-20 \le h \le 20$ $-13 \le k \le 13$ $-12 \le l \le 12$
Reflections collected	28111	8563
Reflections unique	5949	1045
Reflections observed (4σ)	3421	787
R (int.)	0.0767	0.0597
Data/restraints/parameters	5949/0/298	1045/1/128
GOF	1.051	0.997
R_1, wR_2 [$I > 4\sigma(I)$]	0.0419, 0.0937	0.0345, 0.0801
R_1, wR_2 (all data)	0.0726, 0.0988	0.0498, 0.0847

as seen in the coordination of the Na cations by the nitro-groups in the molecular structure.

The ^{1}H NMR spectrum of **2** (Fig. 1) shows two multiplets in the aromatic region corresponding to the phenyl-group hydrogen atoms in the cation, whereas **3** shows a broad and a sharp resonances at 4.57 and 1.97 ppm corresponding to the coordination water and acetonitrile, respectively. The

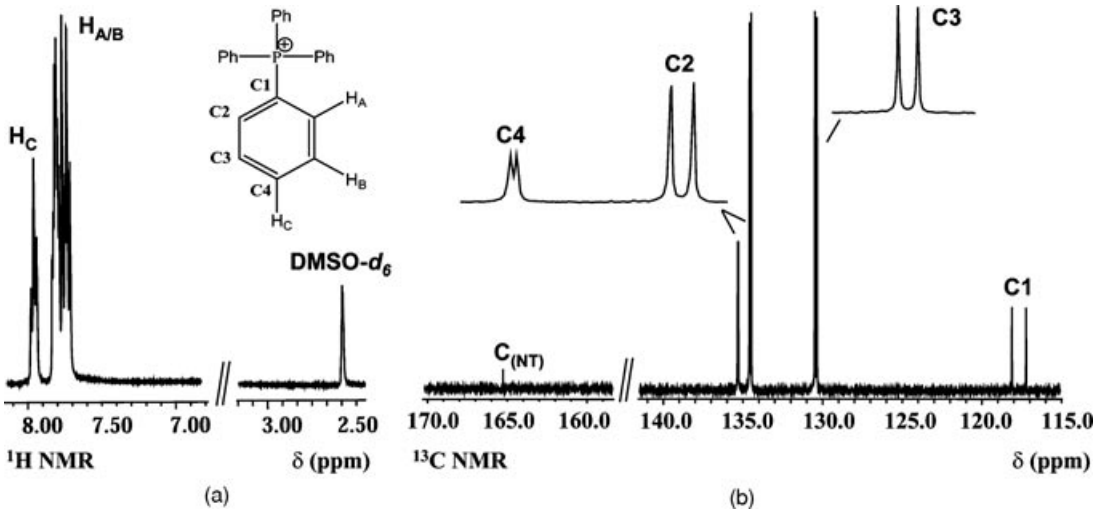


FIGURE 1 (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **2** in DMSO-d_6.

TABLE 2 Distances (Å) and Angles (°) for the 5-Nitrotetrazolate Anion in Compounds **2** and **3**

	2	**3 (A)**	**3 (B)**
N5–O1	1.205(3)	1.226(1)	1.227(1)
N5–O2	1.212(3)	1.226(1)	1.227(1)
N5–C1	1.436(3)	1.441(1)	1.441(1)
N1–N2	1.343(3)	1.354(1)	1.338(1)
N2–N3	1.299(3)	1.319(1)	1.342(1)
N3–N4	1.341(3)	1.354(1)	1.338(1)
C1–N1	1.298(3)	1.325(1)	1.328(1)
C1–N4	1.287(3)	1.325(1)	1.328(1)
	2	**3 (A)**	**3 (B)**
O1–N5–O2	123.0(3)	124.8(3)	125.0(2)
O1–N5–C1	118.2(2)	117.6(2)	117.5(2)
O2–N5–C1	118.8(2)	117.6(2)	117.5(2)
C1–N1–N2	103.7(2)	102.0(2)	103.2(2)
N1–N2–N3	108.6(2)	110.0(2)	109.5(2)
N2–N3–N4	109.6(2)	110.0(2)	109.5(2)
N3–N4–C1	103.4(2)	102.0(2)	103.2(2)
N4–C1–N1	114.7(2)	114.6(3)	115.9(2)
N4–C1–N5	122.8(2)	122.7(2)	122.0(2)
N1–C1–N5	122.5(2)	122.7(2)	122.0(2)

A and B denote two crystallographically independent anions in the crystal structure of **3**.

resonance of the anion carbon atom in the ^{13}C NMR of **2** and **3** has very low intensity and is found at 165.2 ppm in both cases. In addition, **3** shows the expected resonances for the coordinated acetonitrile (see Analytical Data of **3**) and **2** shows the resonances corresponding to the aromatic carbon atoms in the cation in the range between ~118 and ~135 ppm. In addition, Fig. 1 shows the ^{13}C NMR spectra of compound **2**. The coupling constants between the carbon and the phosphorous atoms have the following values: $^{1}J_{C\text{-}P} = 89.2$, $^{2}J_{C\text{-}P} = 10.8$, $^{3}J_{C\text{-}P} = 12.7$, and $^{4}J_{C\text{-}P} = 2.7$ Hz and are useful to assign the carbon atoms resonances by comparison with the literature [22]. Finally, the ^{14}N NMR shows two broad ($\Delta\nu_{1/2}$ ~400 Hz) resonances at ~+20 and ~ −60 ppm corresponding to the tetrazole-ring nitrogen atoms and the nitro-group resonance is much sharper ($\Delta\nu_{1/2}$ ~70 Hz) and found at ~–20 ppm.

The solid-state structures of **2** and **3** were determined experimentally by X-ray diffraction analysis. In Table 2, there are tabulated the distances and angles for the anion in both compounds. Whereas the crystal structure of **2** is composed of one only crystallographically independent anion, that of **3** is composed of two (A and B). The distances and angles in **3** are in agreement with previous reports [6–7], whereas **2** shows, in general, comparatively shorter bonds, indicating a better conjugation of the negative charge throughout the tetrazole ring as expected from the lack of interaction to the cation.

Figure 2 shows the asymmetric unit of **2** with the labeling scheme. As expected in the solid state, there are no interactions between cations and anions due to the great bulk of the tetraphenylphosphonium cations and the lack of hydrogen atoms linked to an electronegative atom to form classical hydrogen bonds. The coordination around the phosphorus atoms is tetrahedral, and the phenyl groups arrange themselves in such a way as to diminish the clashes between the aromatic protons as seen in the structure of compounds, containing the same cation [23]. A further discussion of the bonds and angles in the cation (Table 3) of the cation is omitted here.

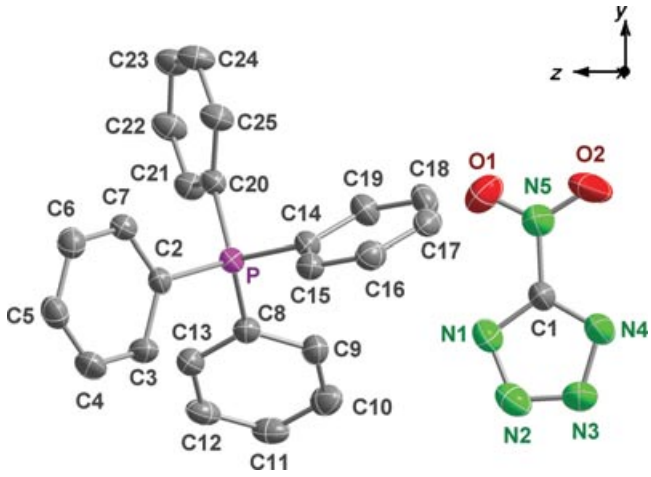


FIGURE 2 Asymmetric unit of **2**, showing the labeling scheme (diamond ellipsoids at the 50% probability). The hydrogen atoms have been omitted for the sake of simplicity.

TABLE 3 Distances (Å) and Angles (°) for the Tetraphenylphosphonium Cation in **2**

Distances (Å)			
P–C1	1.786(2)	C11–C12	1.392(3)
P–C7	1.793(2)	C12–C13	1.387(3)
P–C13	1.793(2)	C13–C14	1.388(3)
P–19	1.791(2)	C14–C15	1.382(3)
C1–C2	1.396(3)	C15–C16	1.376(3)
C3–C2	1.374(3)	C16–C17	1.382(3)
C4–C3	1.386(4)	C17–C18	1.387(3)
C4–C5	1.368(3)	C18–C13	1.394(3)
C6–C5	1.383(3)	C19–C20	1.393(3)
C6–C1	1.392(3)	C20–C21	1.374(3)
C7–C8	1.393(3)	C21–C22	1.387(3)
C8–C9	1.377(3)	C22–C23	1.373(3)
C9–C10	1.378(3)	C23–C24	1.373(3)
C10–C11	1.384(3)	C24–C19	1.393(3)
Angles (°)			
C1–P–C7	110.8(1)	C9–C8–C7	120.0(2)
C1–P–C13	109.9(1)	C16–C15–C14	120.3(2)
C1–P–C19	108.9(1)	C21–C20–C19	120.2(2)
C19–P–C13	109.9(1)	C15–C14–C13	120.1(2)
C19–P–C7	108.3(1)	C17–C18–C13	119.5(2)
C13–P–C7	108.7(1)	C7–C12–C11	119.8(2)
C24–C19–C20	119.3(2)	C16–C17–C18	120.4(2)
C24–C19–P	119.8(1)	C15–C16–C17	120.0(2)
C20–C19–P	120.7(1)	C5–C4–C3	120.8(2)
C10–C11–C12	119.8(2)	C23–C22–C21	120.3(2)
C5–C6–C1	120.1(2)	C4–C5–C6	120.0(2)
C12–C7–C8	119.8(2)	C8–C9–C10	120.2(2)
C12–C7–P	120.8(1)	C2–C3–C4	119.6(2)
C8–C7–P	119.3(2)	C20–C21–C22	119.9(2)
C6–C1–C2	119.1(2)	C9–C10–C11	120.4(2)
C6–C1–P	120.2(2)	C22–C23–C24	120.2(2)
C2–C1–P	120.4(2)	C18–C13–P	120.3(2)
C14–C13–C18	119.7(2)	C23–C24–C19	120.2(2)
C14–C13–P	119.9(2)		

Regardless of the bulk of the cations, there still exists a certain planarity among the 5-nitrotetrazolate anions, which sit on a layer with the nitro-groups pointing toward the opposite direction in respect to the nitro-groups of the anions on the next layer (Fig. 3). The distances between anions layers are approximately ~4 Å, which together with the big cations make for a very inefficient packing. This is reflected in the low-density value ($\rho_{calc} = 1.342$ g/cm^3).

Figure 4 shows a view of the unit cell of **3** along the *y* axis. The two crystallographically independent 5-nitrotetrazolate anions can be distinguished easily: type A anions are found on the vertices of the unit cell, on two of the faces, on four edges and in the center, and they are roughly coplanar to one another and approximately perpendicular to the type B anions, which are found within the unit cell face-on to acetonitrile molecules. The water molecules, which are also found within the unit cell, are linked together through hydrogen bonds to the anions ($d_{O\text{-}N} = 2.899(1)$ Å) and the nitrogen corresponding to an acetonitrile molecule $d_{O\text{-}N} = 3.037(1)$ Å). In Fig. 5, there is represented a view along the *z* axis of the unit cell of the compound. There exists lines of (type A) anions along the *y* axis that interact through π-stacking, and the acetonitrile molecules are coplanar to the plane formed by this type of anions as mentioned above. N3 and O2 (see Fig. 7 for labeling scheme) chelate the Na cations, and these are linked to other cations by coordination to water molecules forming the squares shown in Fig. 5, with lines of anions (type B) perpendicular to it with the axis created by C1 and N5 cutting through two Na atoms.

As shown in Fig. 6, every Na cation coordinates to seven electronegative atoms (four oxygen + three nitrogen atoms), forming a distorted pentagonal bipyramid where the axial positions are occupied by a water molecule and a 5-nitrotetrazolate anion ($\wedge_{O1\text{–}Na1\text{–}N1} = 151.84(1)^\circ$). The rest of the coordination around the metal center is completed on the pentagonal base equatorial "plane" by a second water molecule, two single contacts to two nitrotetrazolates (one to the nitro-group oxygen and

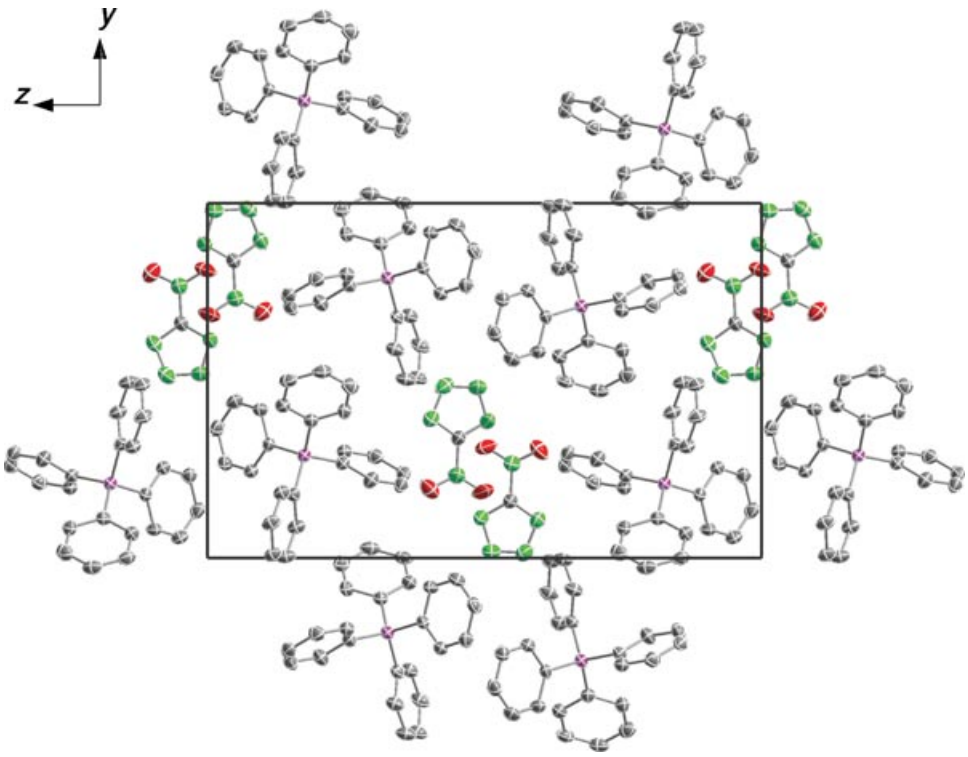


FIGURE 3 View of the unit cell of **2** along the *x* axis (diamond ellipsoids at the 50% probability). The hydrogen atoms have been omitted for the sake of simplicity.

one to a nitrogen atoms) and one nitrotetrazolate, which chelates the Na cation. On the pentagonal base the angles vary between $\wedge_{N2-Na1-N6} = 91.60(1)^\circ$ and $\wedge_{O3-Na1-O5} = 60.30(1)^\circ$ (Table 4).

The two types of crystallographically independent 5-nitrotetrazolate anions are represented in Fig. 7. One of them chelates sodium through N3 and one of the nitro-group oxygen atoms with distances of 2.588(1) and 2.762(1) Å, respectively. A similar chelating effect is also observed for **1**, but is stronger ($d_{N-Na} = 2.467(2)$ Å, $d_{O-Na} = 2.641(2)$ Å) [6]. It can be argued that the insertion of acetonitrile molecules

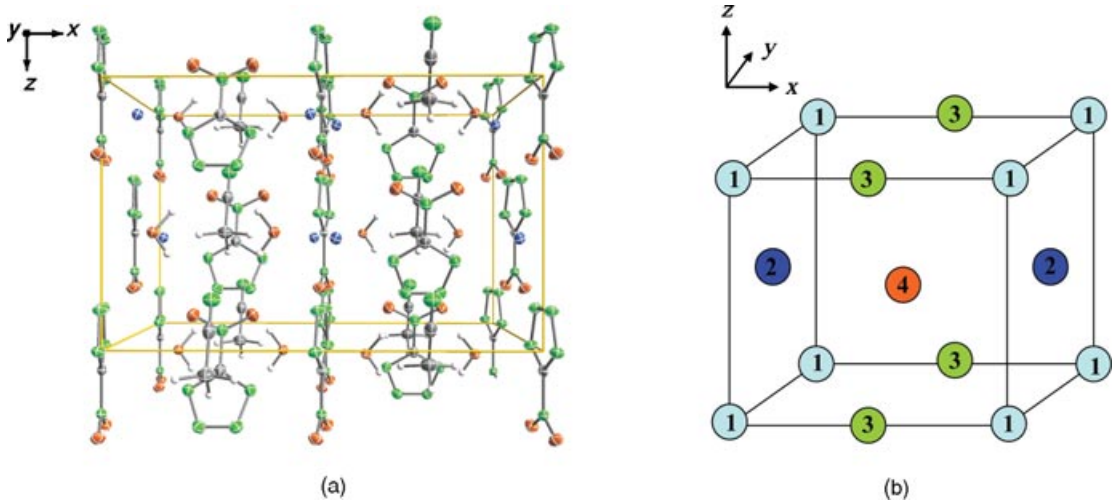


FIGURE 4 Diamond representation (ellipsoids at 50% probability) of a view of the unit cell along the *y* axis in **3** (a) and a schematic representation of the unit cell and (b) 1, 2, 3, and 4 represent 5-nitrotetrazolate anions placed at the edges, in the middle of a face, in the middle of a vertex or in the middle of the cell, respectively.

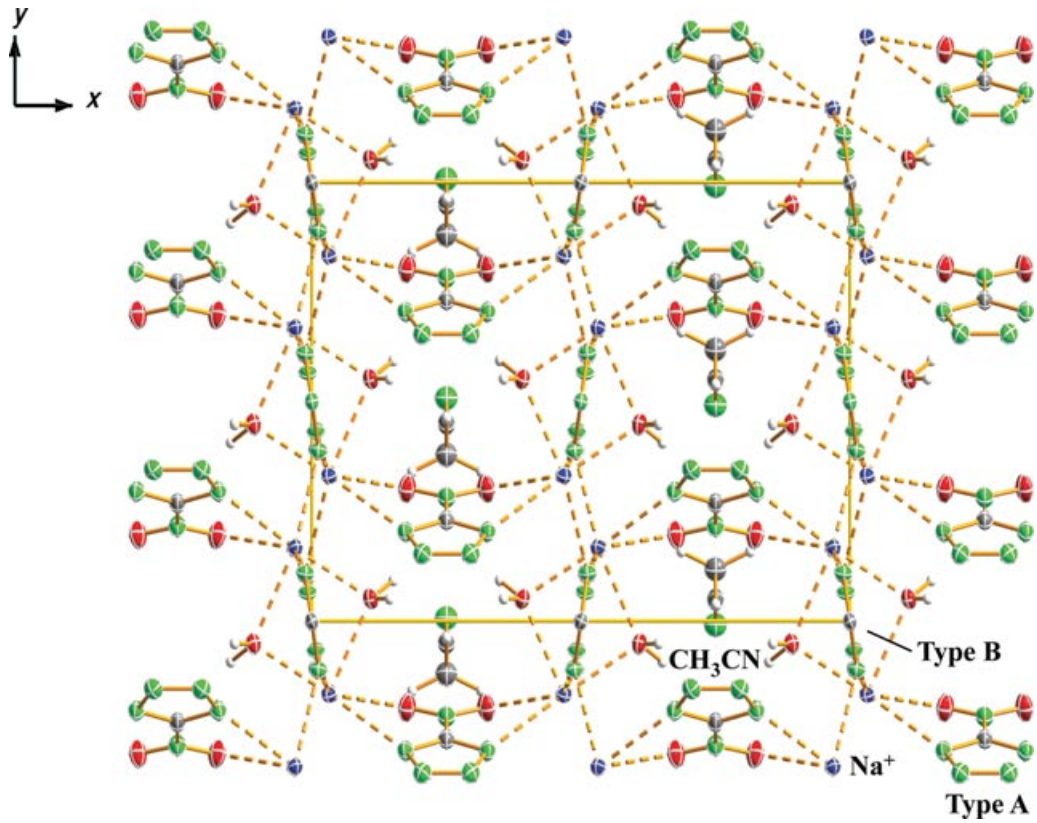


FIGURE 5 View of the unit cell of **3** along the *z* axis, showing the stacks of anions along the *y* axis (diamond ellipsoids at the 50% probability) and the coordination around the Na atoms (dotted lines).

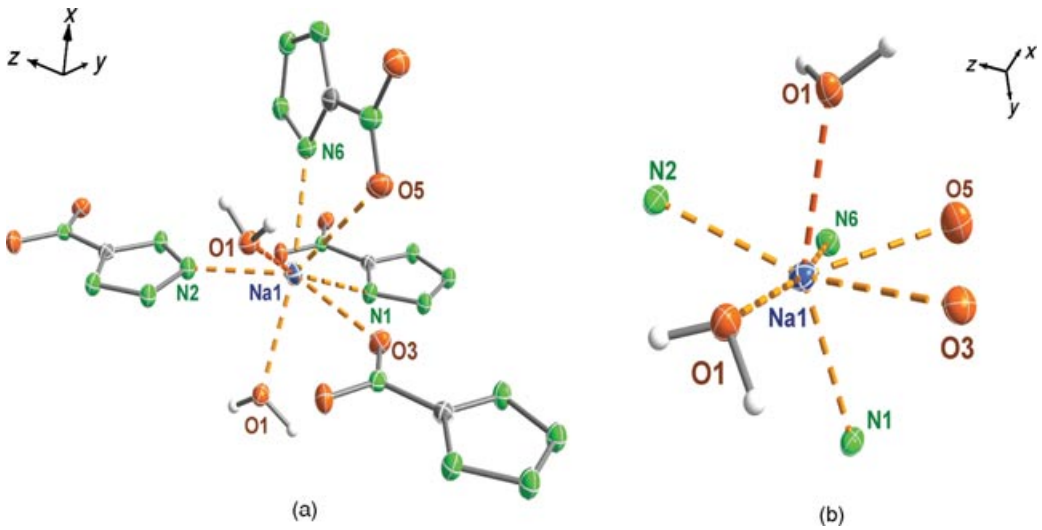


FIGURE 6 Coordination of the sodium atoms in **3** (a) and simplified coordination (b). Diamond ellipsoids at the 50% probability.

in the crystal structure of **2** forces the sodium atoms to place themselves more distant to the nitrotetrazolate anions than when there is no solvent molecules "disturbing" the packing; however, surprisingly, the presence of acetonitrile molecules in the structure of **2** ($\rho_{calc.} = 1.778$ g/cm^3) seems to make for a more efficient overall packing than in the case of **1** where the density calculated from the crystal structure measurement is slightly lower ($\rho_{calc.} = 1.731$ g/cm^3). The other type of anion is characterized by the

TABLE 4 Distances (Å) and Angles (°) for the Coordination Around the Metal Center in **3**

Distances (Å)			
Na–N2	2.527(1)	Na–N6	2.588(1)
Na–O1	2.391(1)	Na–O1	2.454(1)
Na–O3	2.734(1)	Na–N1	2.471(1)
Na–O5	2.763(1)		
Angles (°)			
N2–Na–N6	91.60(1)	O3–Na–O1	74.02(1)
N6–Na–O5	60.77(1)	O1–Na–N2	76.01(1)
O5–Na–O3	60.30(1)	O1–Na–N1	151.84(1)

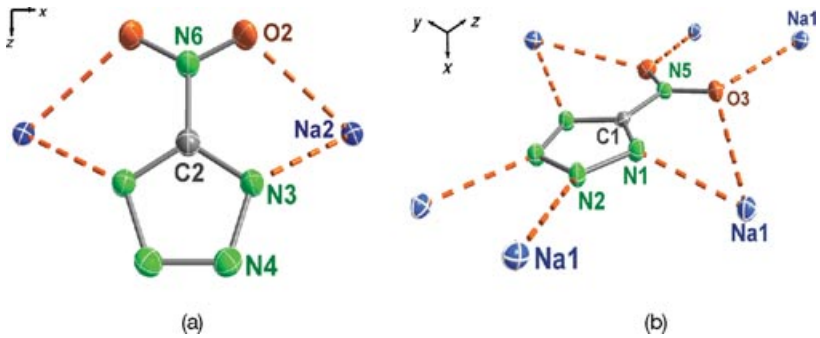


FIGURE 7 Coordination of the 5-nitrotetrazolate anions to cations type A (a) and type B (b) in **3** with the labeling scheme.

coordination to one sodium cation of all electronegative atoms except for the nitro-group nitrogen atom (N5). The strongest coordination is observed, as expected, for the nitrogen atoms ($d_{N1-Na} = 2.471(1)$ Å, $d_{N2-Na} = 2.527(1)$ Å), whereas the oxygen atoms coordinate more loosely with $d_{O-Na} = 2.734(1)$ Å. In comparison to the other crystallographically independent nitrotetrazolate anions, this second type has a much closer bonding to the metal (type A: $d_{N1-Na} = 2.471(1)$ Å, $d_{N2-Na} = 2.527(1)$ Å; type B: $d_{N-Na} = 2.588(1)$ Å).

To assess the energetic properties of **2** and **3**, we measured its sensitivity to shock, friction, and electrostatic discharge by standard BAM tests [24,25] and the thermal stabilities by differential scanning calorimetry (DSC) measurements [12]. Impact: Insensitive >40 J, less sensitive ≥35 J, sensitive ≥4 J, very sensitive ≤3 J; friction: Insensitive >360 N, less sensitive = 360 N, sensitive <360 N a. >80 N, very sensitive ≤80 N, extreme sensitive ≤10 N; According to the *UN Recommendations on the Transport of Dangerous Goods*, (+) indicates: not safe for transport.

At a heating rate of 2°C min^{-1}, **2** melts at ~126°C and decomposes at ~188°C, whereas **3** decomposes at ~200°C. Both compounds showed no sensitivity toward shock (>30 J) nor in the friction test (>360 N). Grinding the compounds in a mortar did not result in explosion either. Both compounds were also insensitive to an electrostatic discharge of ~20 kV, ESD testing using a HF-vacuum-tester type VP 24. Rapid heating of **2** in the flame results in loud explosion, whereas compound **3** burns normally.

In conclusion, we synthesized a salt of 5-nitrotetrazole (**B**) with the bulky tetraphenylphosphonium cation (**2**) and fully characterized it by analytical and spectroscopic methods. The synthesis of highly energetic neutral 2-methyl-5-nitrotetrazole failed, and single crystals of explosive bis-(sodium 5-nitrotetrazolate) dihydrate acetonitrile adduct (**3**) were obtained. Both compounds showed decreased sensitivity to classical stimuli. Finally, the crystal structures of **2** and **3** were determined by X-ray diffraction techniques and are discussed in detail.

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