4,4',5,5'-tetraamino-3,3'-azo-bis-1,2,4-triazole and the electrosynthesis of high-performing insensitive energetic materials

Joseph R. Yount [a], Matthias Zeller [c], Edward F.C. Byrd [d] & Davin G. Piercey.*[a][b]

[a] J. R. Yount, Prof. Dr. D.G. Piercey.
Department of Materials Engineering, Purdue Energetics Research Center
Purdue University
205 Gates Road, West Lafayette, IN 47907, USA
E-mail: dpiercey@purdue.edu
[b] Prof. Dr. D.G. Piercey.
Department of Mechanical Engineering, Purdue Energetics Research Center
Purdue University
205 Gates Road, West Lafayette, IN 47907, USA
[c] Dr. M. Zeller.
Department of Chemistry
Purdue University
560 Oval Drive West Lafayette, IN 47907, USA U.S.
[d] Dr. E.F.C Byrd.
Army Research Laboratory,
Aberdeen Proving Ground, MD 21005, USA

1. Methods

General: All reagents and solvents were used as received (Sigma– Aldrich, Fluka, Acros Organics, Fisher Scientific Co LLC) if not stated otherwise. Guanazine, 5-nitrimino-1,2,3,4-tetrazole and 5-nitro-1,2,3,4-tetrazole were prepared according to literature.[1,2,3] Melting and decomposition points were measured with a TA Instruments SDT Q600 TGA/ DSC using heating rates of 10 K·min^{-1}. ^{1}H and ^{13}C NMR spectra were measured using Bruker AV-III-400-HD (5 mm BBFO SmartProbe) and Bruker AV-III-500-HD (5 mm BBFO Cryoprobe Prodigy) Avance DRX NMR spectrometers. All chemical shifts are quoted in ppm relative to TMS (1 H, 13C). Infrared spectra were measured using a Perkin– Elmer Spectrum Two FT-IR spectrometer. Transmittance values are described as "strong" (s), "medium" (m) and "weak" (w). Mass spectra were measured with an Agilent 1260 Infinity II Quaternary LC instrument. Elemental analysis was performed using the Vario EL cube – Elemental Analyzer. Sensitivity data were determined using a BAM friction tester (Reichel & Partner GmbH) and OZM drophammer. CV and electrolysis experiments were performed using an IKA Electrosyn 2.0. [4]

CAUTION! The described compounds 2-7 are energetic materials with sensitivity to various

stimuli. While we encountered no issues in the handling of these materials, proper protective measures (face shield, ear protection, body armor, Kevlar gloves, and earthened equipment) should be used at all times.

General Procedures for CV

Cyclic voltammograms (CV) were taken using an IKA Electrosyn 2.0 instrument equipped with an Ag/AgCl reference electrode, a 3mm glassy carbon working electrode, and a carbon counter electrode. The glassy carbon working electrode was polished prior to each run using a procedure outlined by Dempsey *et al*.[5] Solutions were purged with Ar gas prior to each run to remove oxygen. Ar gas was purged over the top of the solution to keep a blanket during the runs. CV experiments were performed at variable scan rates and over multiple cycles. Electrolysis of guanazine was carried out using a two-electrode set up on an Electrosyn 2.0. All electrolysis experiments were performed under constant potential conditions using a carbon (580 cm^2) working and Pt foil (232 cm^2) counter electrode.

After electrolysis all solutions were sonicated to create a slurry and then transferred to a falcon tube with minimal water. The slurry was centrifuged at 4000 rpms for 10 minutes. The supernatant was removed, and product was washed with water to remove unreacted guanazine and electrolyte. The supernatant collected was monitored using LC-MS to determine the number of washes necessary to remove excess guanazine and electrolyte. It was found that a single wash with 30 mL of milli-pure DI water was adequate to attain a pure sample. The concentrated solid was dried under an airline and kept in a desiccator to remove adsorbed water.

General Procedures for X-ray crystallographic data collection

Data for single crystals of compounds **2a•H_2O**, **2b•H_2O**, **3**, **4•H_2O**, **5•H_2O**, and **7** were collected using a Bruker Quest diffractometer with a fixed chi angle, a Mo Kα wavelength (λ = 0.71073 Å) sealed tube fine focus X-ray tube, a single crystal curved graphite incident beam

monochromator, and either a Photon100 (**2a•H_2O**, **2b•H_2O**, **4•H_2O**, **5•H_2O**, **7**)or a Photon2 CMOS area detector (**3**). Data for single crystals of compounds **5**, **6•4H_2O** and **6•MeOH •0.5$C_4H_8N_{12}$** were collected using a Bruker Quest diffractometer with kappa geometry, a Cu Kα wavelength (λ = 1.54178 Å) I-μ-S microsource X-ray tube, laterally graded multilayer (Goebel) mirrors for monochromatization, and a Photon2 CMOS area detector. Both instruments were equipped with an Oxford Cryosystems low temperature device and examination and data collection were performed at 150 K. Data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3, SAINT and SADABS or TWINABS.[6,7] The space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs and refined by full matrix least squares against F^2 with all reflections using Shelxl2018 using the graphical interface Shelxle.[8,9]

(1) 3,4,5-triamino-1,2,4-triazole

Was synthesized according to the literature procedure.[36] ^{1}H NMR (dmso-d_6) δ(ppm)=5.15(s, 2H), 5.03 (s, 4H); 13 C NMR (dmso-d_6) δ(ppm)=151.31(2C)

(2) 4,4',5,5'- tetra-amino-3,3'-azo bis-1,2,4-triazole (TAABT)

200 mg of guanazine in 10 mL of 0.1 M $(NH_4)_2CO_{3(aq)}$ was electrolyzed at 2.5 V in a single compartment cell using a carbon (580 cm^2) working and Pt foil (232 cm^2) counter electrode until 2 F/mol of charge was passed. The slurry was then sonicated, centrifuged, washed three times to remove excess precursor. The sample was then dried in a desiccator over P_2O_5 to yield 4,4',5,5' tetra-amino-3,3'-azo bis-1,2,4-triazole monohydrate **2•H_2O** at 40.2% yield.

^{13}C NMR (dmso-d_6) δ(ppm)=157.53(2C), 156.07(2C); ^{1}H NMR (dmso-d_6) δ(ppm)= 6.43(s, 4H), 5.86(s, 4H); EA: ($C_4H_8N_{12}$.H_2O, 242.2020 g/mol) calcd: 69.40 % N, 19.84 % C,4.16% H, found: 66.23% N, 19.22% C, 4.48% H; DSC (10°C min^{-1}) T_{Dec} at 291°C; IR (cm^{-1}) ν = 3289.78(w), 3111.19(w), 1564.64(s), 1546.94(s), 1448.94(s), 1375.87(w), 1274.40(w), 1072.02(s), 956.93(s), 826.14(w), 809.45(w), 749.87(m), 619.94(s), 548.52(m); MS (MALDI): m/z: 226.2 ($C_4H_{10}N_{12}^{2+}$); BAM impact: >40J; BAM friction >360N.

100 mg of TAABT•H_2O was added to a 25mL round bottom flask and placed onto a high vacuum Schlenk line. The sample was placed under < 1 mbar pressures while being heated at 90 °C overnight. The dried sample was identified as anhydrous TAABT by elemental analysis (100% yield).

^{13}C NMR (dmso-d_6) δ(ppm)=157.53(2C), 156.07(2C); ^{1}H NMR (dmso-d_6) δ(ppm)= 6.43(s, 4H), 5.86(s, 4H); EA: ($C_4H_8N_{12}$, 224.19 g/mol) calcd: 74.9734% N, 21.4298% C, 3.5968% H, found: 74.94% N, 22.09% C, 4.00% H; DSC (10°C min^{-1}) T_{Dec} at 302 °C; IR (cm^{-1}) ν =3297.75(w), 3075.30(w), 1645.34(m), 1540.12(m), 147.75(m), 1376.01(w), 1322.53(w), 121.00(w), 1066.54(s), 960.86(m), 815.72(m), 760.28(m), 724.80(m), 692.55(m), 615.42(m), 541.92(m), 464.87(w); BAM impact: >40J; BAM friction >360N.

(3) 4,4',5,5' tetra-amino-3,3'-azo bis-1,2,4-triazolium dinitrate

1.338 g (0.014 mol) of concentrated (15.8M) nitric acid was added to a beaker containing 100 mg (0.00041mol) of TAABT•H_2O in DI H_2O, representing a 34 mol eq. of HNO_3. The solution was stirred at room temperature until TAABT was fully dissolved. The solution was then allowed to slowly evaporate yielding orange crystals. After filtration and drying 103 mg of sample was collected (86.8% yield).

^{13}C NMR (DMSO-d_6) δ(ppm)= 154.91(2C), 152.56(2C)**;** ^{1}H NMR (DMSO-d_6) δ(ppm)= 8.27(s, 2H), 6.31(broad s, 5H); EA: ($C_4H_{10}N_{12}$•2(NO_3), 350.21g/mol) calcd: 55.99% N, 13.72% C, 2.88% H, found 56.53% N, 13.59% C, 2.93% H. DSC (10°C min^{-1}): 234 °C ($T_{Dec,\ onset}$); IR (cm^{-1}) ν = 3347.85(w), 3103.20(w), 1687.75 (m), 1601.32(w), 1532(w), 1433.87(m),1313.47(s), 1255.92(m), 1128.10(m), 1069.85(w), 1040.09(m), 972.61(w), 859.61(w), 804.75(m), 713.88(w), 664.32(m); MS (ESI +): m/z: 225.2 ($C_4H_9N_{12}^{+}$); MS (ESI-):m/z: 62.1 (NO_3^{-}); BAM impact: <1 J; BAM friction 64-80 N.

(4) 4,4',5,5' tetra-amino-3,3'-azo bis-1,2,4-triazolium nitrate

97 mg of TAABT•H_2O was combined with 43 mg of conc. HNO_3 (1.12 mol eq.) in 20 mL of DI water. This slurry was stirred at room temperature for 3 days yielding a light orange slurry. The

mixture was then filtered and washed with 2-propanol. This was then recrystallized in water yielding the monohydrate mononitrate **4•H_2O**. The remaining salt was then dried under high vacuum (< 1 mbar) on a Schlenk over night while being heated at 90 ºC. The isolated product was identified as anhydrous **4**. No product was lost during drying, so yield was assumed to be 100%. The sample was removed from the vacuum, sealed with parafilm, and stored in a desiccator prior to use.

^{13}C NMR (DMSO-d_6) δ(ppm)= 155.53(4C); ^{1}H NMR (DMSO-d_6) δ(ppm)= 7.78(s, 4H), 6.16(broad s, 4H); EA: ($C_4H_9N_{12}$•NO_3, 287.1996 g/mol) calcd: 63.40% N, 16.73% C, 3.16% H, found 63.33% N, 16.93% C, 3.83% H; DSC (10°C min^{-1}) T_{Dec} at 230 °C; IR (cm^{-1}) ν =3428.72(w), 3319.78(w), 3152.04(w), 1685.75(m), 1629.69(m), 1542.43(w), 1501.71(m), 1389.36(m), 1348.91(m), 1309.38(s), 1278.24(m), 1133.22(w), 1105.27(s), 1022.38(m), 893.59(w), 824.50(m), 767.03(w), 731.43(w), 691.73(w), 567.92(m); BAM impact: >40J; BAM friction >360N.

(5) 4,4',5,5' tetra-amino-3,3'-azo bis-1,2,4-triazolium perchlorate

203 mg of TAABT was combined with a 1.72 mol eq. of 60% $HClO_4$ (240 mg) in water. The solution was stirred with heat until the azo complex was completely dissolved. The solution was allowed to slowly evaporate yielding red crystals of the monohydrate **5•H_2O**. DSC and elemental analysis results show a loss of the water of hydration. After filtration and drying in dessicator,184 mg of light orange crystals of anhydrous **5** were collected (67.6% yield). The crystal structure of anhydrous **5** was determined by single crystal x-ray diffraction re-crystallization in MeOH.

^{13}C NMR (DMSO-d_6) δ(ppm)= 155.54(4C); ^{1}H NMR (DMSO-d_6) δ(ppm)= 7.80(s, 4H), 6.04(broad s, 4H); EA: ($C_4H_9N_{12}$•ClO_4, 324.6453g/mol) calcd: 51.77% N, 14.80% C, 2.79% H, found: 51.79% N, 14.46% C, 2.72% H; DSC (10°C min^{-1}) 254 °C ($T_{Dec, onset}$); IR (cm^{-1}) ν = 3459.68(w), 3361.38(w), 3324.09(m), 1662.50(m), 1606.98(m), 1527.13(w), 1358.92(w), 1069.95(s), 975.40(m), 864.14(m), 764.30(m), 720.7(m), 620.46(s); MS (ESI +): m/z: 225.2 ($C_4H_9N_{12}^{+}$); MS (ESI-):m/z: 99.1 (ClO_4^{-}); BAM impact: <1 J; BAM friction 128 N.

(6) 4,4',5,5' tetra-amino-3,3'-azo bis-1,2,4-triazolium 5-nitrimino-1,2,3,4-tetrazolate monohydrate

An equal molar solution of 5-nitriminotetrazole (162 mg) and TAABT (200 mg) in 100 mL of milli-pore water was heated at 70 °C until the solution became clear. The solution was then allowed to slowly evaporate and crystalize to yield fine red needle crystals of compound **6•4H_2O** in the form of the tetrahydrate as confirmed by X-ray diffraction. DSC and elemental analysis results show a loss of 3 waters of hydration yielding the monohydrate salt. After filtration and drying in a desiccator over P_2O_5 218 mg of monohydrate **10** were collected (70.8% yield). The crystal structure of **6•MeOH •0.5$C_4H_8N_{12}$** a cocrystal of **6•MeOH** with unprotonated (**2**) was determined by single crystal x-ray diffraction as its monomethanol solvate.

^{1}H NMR (DMSO-d_6) δ(ppm)= 7.77(s, 4H), 6.04(s, 4H); EA: ($C_4H_9N_{12}$•CN_5O_2•H_2O, 372.27 g/mol) calcd: 67.73% N, 16.13% C, 3.25% H, found: 67.48% N, 16.14% C, 3.36% H; DSC (10°C min^{-1}) 219 °C ($T_{Dec,\ onset}$); IR (cm^{-1}) ν =3560.35(w), 3019.19(w), 1704.98(m), 1647.53(m), 1533.38(m), 1431.87(m), 1368.20(w), 1313.99(s), 1270.93(m), 1221.44(m), 1095.24(m), 1071.99(m), 1042.95(m), 966.49(m), 649.95(m), 533.67(s), 473.04(s); MS (ESI +): m/z: 225.2 ($C_4H_9N_{12}^+$); MS (ESI-):m/z: 129.1 ($CHN_6O_2^-$); BAM impact: >40 J; BAM friction >360 N.

(7) 4,4',5,5' tetra-amino-3,3'-azo bis-1,2,4-triazolium di-5-nitro-1,2,3,4-tetrazolate

A molar excess of sodium 5-nitrotetrazolate salt was prepared in aqueous solution and acidified to pH ~1 with concentrated sulfuric acid. This was then extracted with 7 x 40 mL of ethyl acetate. The combined ethyl acetate washes were added to a slurry of 200 mg of TAABT in 100 mL of millipore water. The solution was stirred under an airline to remove excess ethyl acetate until all remaining ethyl acetate had fully evaporated combining the 5-nitrotetrazole and TAABT in the remaining solvent. The solution was heated at 70 ºC with stirring to fully dissolve TAABT. Only slight heating was required due to the strong acidity of 5-nitrotetrazolate. The solution was then allowed to slowly evaporate and crystallize. After filtration and drying in a desiccator over P_2O_5 244 mg of salt were collected. (64.5% yield)

^{13}C NMR (DMSO-d_6) δ(ppm)= 154.96(2C), 154.63(2C); ^{1}H NMR (DMSO-d_6) δ(ppm)= 8.25(s, 2H), 6.21(broad s, 5H); EA: ($C_6H_{10}N_{22}O_4$•2(CN_5O_2), 454.29 g/mol) calcd: 67.83% N, 15.86% C, 2.22% H, found: 69.12% N, 15.91% C, 2.24% H; DSC (10°C min^{-1}) 240 °C ($T_{Dec, onset}$); IR (cm^{-1}) ν =3349.00(w), 3059.87(w), 2691.81(w), 1696.20(s), 1634.97(w), 1537.78(m), 1446.88(m), 1423.48(s), 1372.48(m), 1321.94(s), 1281.68(m), 1182.51(s), 1161.77(s), 1143.14(m), 1082.49(m), 1034.77(w), 979.20(s), 838.95(s), 798.49(m), 765.05(m), 765.05(m), 664.37(m), 636.26(m), 535.05(s), 571.56(s), 458.66(m); MS (ESI +): m/z: 225.2 ($C_4H_9N_{12}^+$); MS (ESI-):m/z: 114.1 ($CN_5O_2^-$); BAM impact: >40 J; BAM friction 116 N.

2. X-ray diffraction

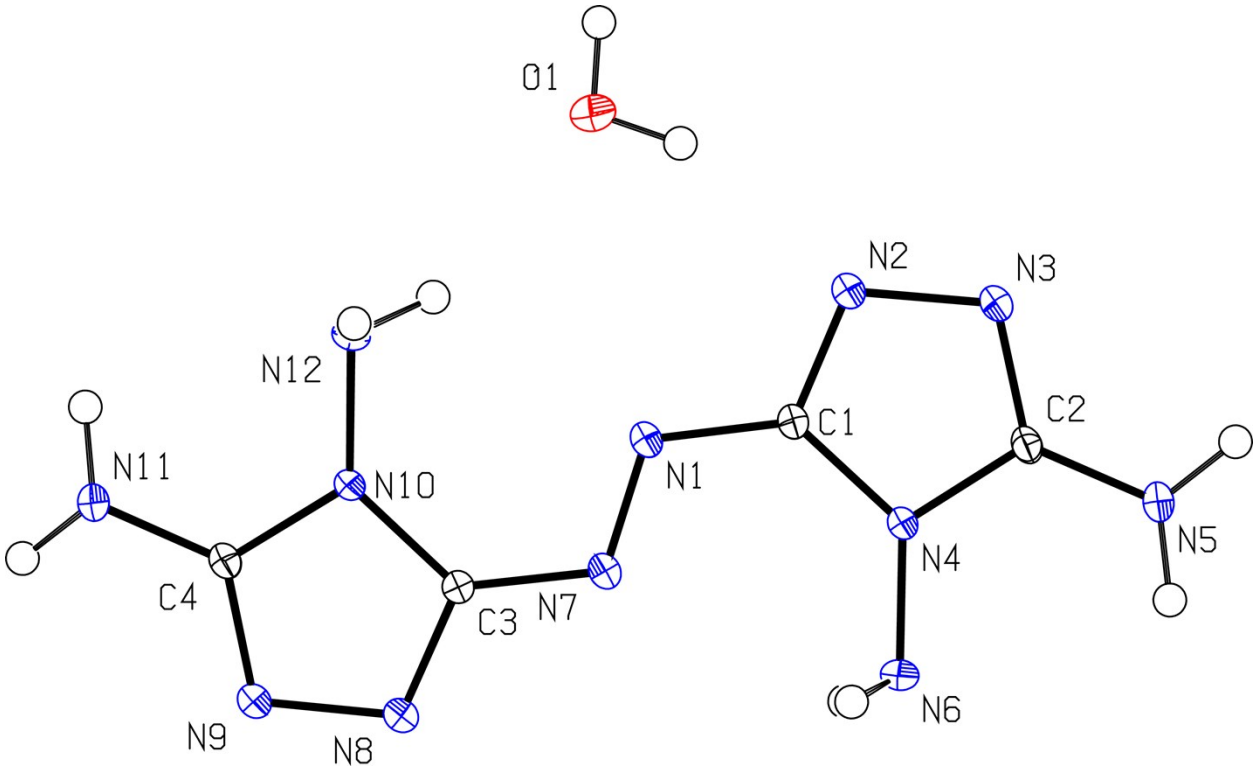
For general procedures, see Methods section.

Hydrogen Atom Treatment

For compounds **2a•H_2O**, **2b•H_2O**, **3**, **5•H_2O**, **5** and **7** H atoms were located from difference density Fourier maps and their positions and isotropic displacement parameters were freely refined. For **5**, amine N-H bonds were restrained to be similar in length. In **5**, the ammonium H atom is located on a two-fold axis and is shared between two symmetry equivalent N atoms. In compounds **4•H_2O**, **6•4H_2O** and **6•MeOH $C_4N_{12}H_8$**, H atoms attached to sp^2 hybridized nitrogen atoms were positioned geometrically and constrained to ride on their parent atoms with N-H bond distances constrained to 0.88 Å. All other N-bound H atoms were located from difference density Fourier maps and refined and N-H bond distances were restrained to 0.88(2) Å. In **4•H_2O**, H···H distances in NH_2 groups were restrained to a target value of 1.36(2) Å. CH_3 C-H bond distances were constrained to 0.98 Å, alcohol O-H distances to 0.84 Å. Methyl CH_3 and hydroxyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. Water O-H distances were restrained to 0.84(2) and H···H distances to 1.36(2) Å. U_{iso}(H) values for **4•H_2O**, **6•4H_2O** and **6•MeOH $C_4N_{12}H_8$** were

set to a multiple of U_{eq}(C/N/O) with 1.5 for CH_3, NH_3^+ and OH, and 1.2 for N-H^+, N-H and NH_2 units, respectively.

Single Crystal XRD data for 4,4',5,5' tetra-amino-3,3'-azo bis-1,2,4-triazole monohydrate (TAABT•H_2O) (2a•H_2O)



View of the structure of **2a•H_2O**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Crystal data

$C_4H_8N_{12}·H_2O$	Z = 2
M_r = 242.24	F(000) = 252
Triclinic, $P\bar{1}$	D_x = 1.626 Mg m^{-3}
a = 7.9678 (5) Å	Mo $K\alpha$ radiation, λ = 0.71073 Å
b = 8.1421 (5) Å	Cell parameters from 8021 reflections
c = 8.4183 (6) Å	θ = 2.6–33.2°
α = 89.448 (2)°	μ = 0.13 mm^{-1}
β = 69.466 (2)°	T = 150 K

$\gamma = 76.132\ (2)°$	Plate, orange
$V = 494.86\ (6)\ Å^3$	0.45 × 0.25 × 0.18 mm

Data collection

Bruker AXS D8 Quest CMOS diffractometer	12648 measured reflections
Radiation source: fine focus sealed tube X-ray source	3727 independent reflections
Triumph curved graphite crystal monochromator	3189 reflections with $I > 2\sigma(I)$
Detector resolution: 10.4167 pixels mm^{-1}	$R_{int} = 0.026$
ω and phi scans	$\theta_{max} = 33.2°$, $\theta_{min} = 2.6°$
Absorption correction: multi-scan, *SADABS 2016/2, Krause et al., 2015*	$h = -11 \rightarrow 12$
$T_{min} = 0.691$, $T_{max} = 0.747$	$k = -10 \rightarrow 12$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.033$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.093$	All H-atom parameters refined
$S = 1.07$	$w = 1/[\sigma^2(F_o^2) + (0.0499P)^2 + 0.0929P]$ where $P = (F_o^2 + 2F_c^2)/3$
3727 reflections	$(\Delta/\sigma)_{max} < 0.001$
194 parameters	$\Delta\rho_{max} = 0.48\ e\ Å^{-3}$
0 restraints	$\Delta\rho_{min} = -0.28\ e\ Å^{-3}$

Geometric parameters (Å, º) for 2a•H_2O

O1–H1A	0.840 (16)	N6–H6B	0.903 (13)
O1–H2B	0.858 (16)	N7–C3	1.3712 (9)
N1–N7	1.2797 (8)	N8–C3	1.3186 (9)
N1–C1	1.3734 (9)	N8–N9	1.3692 (9)
N2–C1	1.3176 (9)	N9–C4	1.3387 (9)
N2–N3	1.3771 (9)	N10–C4	1.3624 (9)
N3–C2	1.3430 (9)	N10–C3	1.3844 (9)
N4–C2	1.3649 (9)	N10–N12	1.4118 (8)
N4–C1	1.3870 (9)	N11–C4	1.3417 (9)
N4–N6	1.4076 (8)	N11–H11A	0.896 (14)
N5–C2	1.3341 (9)	N11–H11B	0.873 (15)

N5–H5A	0.919 (13)	N12–H12A	0.900 (14)
N5–H5B	0.911 (15)	N12–H12B	0.901 (13)
N6–H6A	0.892 (14)		
H1A–O1–H2B	104.8 (14)	C4–N11–H11A	117.9 (8)
N7–N1–C1	114.56 (6)	C4–N11–H11B	115.4 (9)
C1–N2–N3	108.19 (6)	H11A–N11–H11B	119.3 (12)
C2–N3–N2	107.09 (6)	N10–N12–H12A	109.3 (8)
C2–N4–C1	105.00 (6)	N10–N12–H12B	106.9 (8)
C2–N4–N6	123.30 (6)	H12A–N12–H12B	106.5 (11)
C1–N4–N6	131.69 (6)	N2–C1–N1	119.98 (6)
C2–N5–H5A	119.6 (8)	N2–C1–N4	109.79 (6)
C2–N5–H5B	118.2 (9)	N1–C1–N4	130.21 (6)
H5A–N5–H5B	120.7 (12)	N5–C2–N3	125.75 (7)
N4–N6–H6A	106.0 (9)	N5–C2–N4	124.30 (6)
N4–N6–H6B	107.2 (8)	N3–C2–N4	109.92 (6)
H6A–N6–H6B	106.1 (12)	N8–C3–N7	120.16 (6)
N1–N7–C3	113.78 (6)	N8–C3–N10	109.40 (6)
C3–N8–N9	108.54 (6)	N7–C3–N10	130.39 (6)
C4–N9–N8	106.96 (6)	N9–C4–N11	125.89 (6)
C4–N10–C3	105.00 (6)	N9–C4–N10	110.09 (6)
C4–N10–N12	122.38 (6)	N11–C4–N10	123.91 (6)
C3–N10–N12	132.51 (6)		
C1–N2–N3–C2	0.65 (8)	N6–N4–C2–N3	-178.49 (6)
C1–N1–N7–C3	-178.23 (6)	N9–N8–C3–N7	-178.31 (6)
C3–N8–N9–C4	0.08 (8)	N9–N8–C3–N10	-0.62 (8)
N3–N2–C1–N1	-179.09 (6)	N1–N7–C3–N8	171.44 (7)
N3–N2–C1–N4	-0.34 (8)	N1–N7–C3–N10	-5.70 (11)
N7–N1–C1–N2	-179.46 (7)	C4–N10–C3–N8	0.90 (8)
N7–N1–C1–N4	2.07 (11)	N12–N10–C3–N8	177.08 (7)
C2–N4–C1–N2	-0.10 (8)	C4–N10–C3–N7	178.27 (7)
N6–N4–C1–N2	178.79 (7)	N12–N10–C3–N7	-5.54 (13)
C2–N4–C1–N1	178.49 (7)	N8–N9–C4–N11	-175.87 (7)
N6–N4–C1–N1	-2.62 (13)	N8–N9–C4–N10	0.50 (8)
N2–N3–C2–N5	177.54 (7)	C3–N10–C4–N9	-0.85 (8)

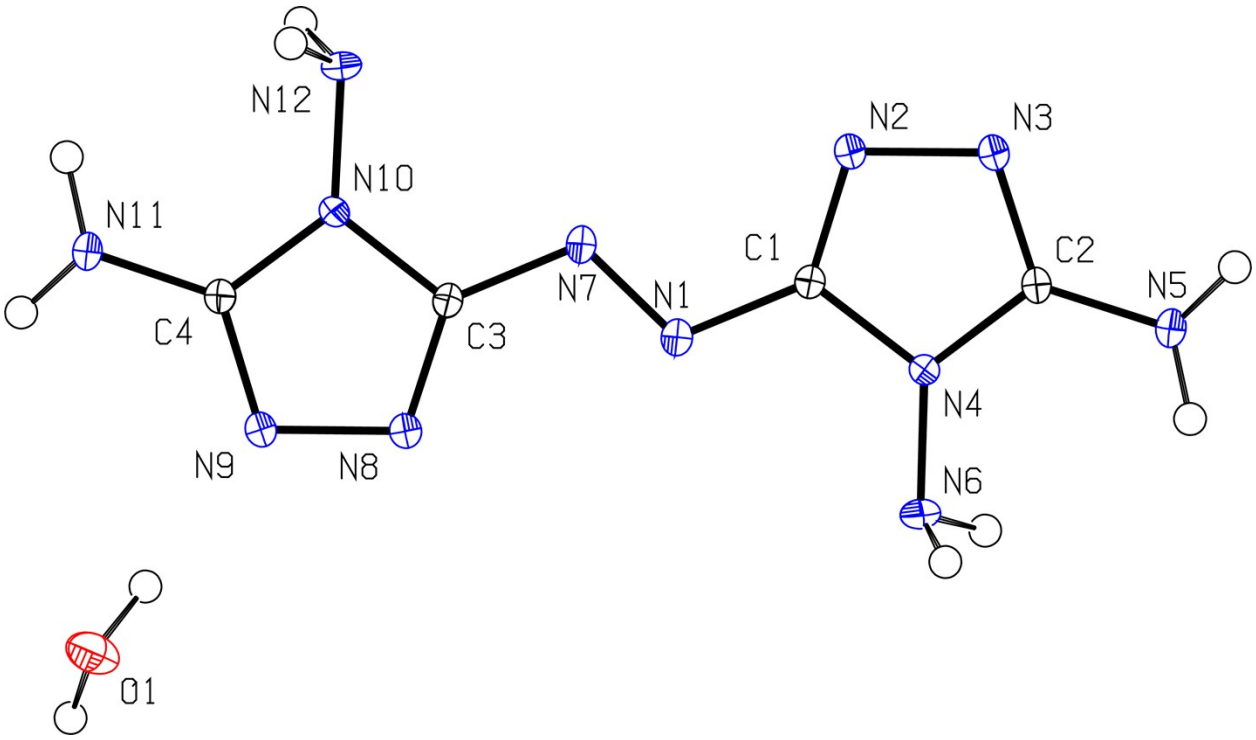
N2–N3–C2–N4	-0.73 (8)	N12–N10–C4–N9	-177.52 (6)
C1–N4–C2–N5	-177.78 (7)	C3–N10–C4–N11	175.60 (7)
N6–N4–C2–N5	3.20 (11)	N12–N10–C4–N11	-1.06 (11)
C1–N4–C2–N3	0.52 (8)		

Hydrogen-bond geometry (Å, º) for 2a•H_2O

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
O1–H1*A*···N8^{i}	0.840 (16)	1.945 (16)	2.7563 (9)	162.2 (14)
O1–H2*B*···N2	0.858 (16)	2.120 (16)	2.9284 (9)	156.7 (15)
N5–H5*A*···N12^{ii}	0.919 (13)	2.348 (13)	3.1678 (9)	148.5 (11)
N5–H5*B*···N9^{iii}	0.911 (15)	2.055 (15)	2.9456 (9)	165.4 (13)
N6–H6*A*···N3^{iv}	0.892 (14)	2.646 (13)	3.2690 (10)	127.7 (11)
N6–H6*B*···O1^{v}	0.903 (13)	2.146 (13)	3.0139 (10)	160.9 (12)
N11–H11*A*···N6^{vi}	0.896 (14)	2.280 (14)	3.0709 (9)	147.2 (11)
N11–H11*B*···N3^{vii}	0.873 (15)	2.126 (15)	2.9694 (9)	162.3 (13)
N12–H12*A*···O1	0.900 (14)	2.289 (14)	3.1208 (9)	153.6 (11)
N12–H12*A*···N1	0.900 (14)	2.383 (13)	2.9213 (9)	118.5 (10)
N12–H12*B*···O1^{viii}	0.901 (13)	2.151 (13)	3.0324 (10)	165.8 (12)

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) *x*-1, *y*+1, *z*; (iii) *x*-1, *y*+1, *z*+1; (iv) -*x*, -*y*+1, -*z*+1; (v) -*x*, -*y*, -*z*+1; (vi) *x*+1, *y*-1, *z*; (vii) *x*+1, *y*-1, *z*-1; (viii) -*x*+1, -*y*, -*z*+1.

***Single Crystal XRD data for 4,4',5,5' tetra-amino-3,3'-azo bis-1,2,4-triazole monohydrate (TAABT•H_2O)* (2b•H_2O)**



View of the structure of **2b•H_2O**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Crystal data

$C_4H_8N_{12}·H_2O$	$F(000)$ = 504
M_r = 242.24	D_x = 1.723 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 11.0909 (7) Å	Cell parameters from 6377 reflections
b = 12.0277 (7) Å	θ = 2.5–33.1°
c = 7.0869 (5) Å	μ = 0.14 mm^{-1}
β = 99.011 (3)°	T = 150 K
V = 933.71 (10) Å^3	Rod, red
Z = 4	0.35 × 0.11 × 0.10 mm

Data collection

Bruker AXS D8 Quest CMOS diffractometer	24491 measured reflections
Radiation source: fine focus sealed tube X-ray source	3582 independent reflections

Triumph curved graphite crystal monochromator	2373 reflections with $I > 2\sigma(I)$
Detector resolution: 10.4167 pixels mm^{-1}	$R_{int} = 0.063$
ω and phi scans	$\theta_{max} = 33.2°$, $\theta_{min} = 2.5°$
Absorption correction: multi-scan, *SADABS 2016/2, Krause et al., 2015*	$h = -17 \rightarrow 17$
$T_{min} = 0.694$, $T_{max} = 0.747$	$k = -18 \rightarrow 18$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.049$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.133$	All H-atom parameters refined
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (0.0648P)^2 + 0.2487P]$ where $P = (F_o^2 + 2F_c^2)/3$
3582 reflections	$(\Delta/\sigma)_{max} < 0.001$
194 parameters	$\Delta\rho_{max} = 0.47$ e $Å^{-3}$
0 restraints	$\Delta\rho_{min} = -0.45$ e $Å^{-3}$

Geometric parameters (Å, º) for 2b•H_2O

O1–H1A	0.90 (3)	N6–H6B	0.92 (2)
O1–H1B	0.90 (3)	N7–C3	1.3827 (16)
N1–N7	1.2742 (15)	N8–C3	1.3140 (17)
N1–C1	1.3825 (17)	N8–N9	1.3829 (15)
N2–C1	1.3182 (17)	N9–C4	1.3370 (16)
N2–N3	1.3754 (15)	N10–C4	1.3584 (17)
N3–C2	1.3370 (16)	N10–C3	1.3803 (16)
N4–C2	1.3550 (17)	N10–N12	1.3976 (15)
N4–C1	1.3780 (16)	N11–C4	1.3492 (17)
N4–N6	1.4032 (15)	N11–H11A	0.927 (19)
N5–C2	1.3469 (17)	N11–H11B	0.88 (2)
N5–H5A	0.89 (2)	N12–H12A	0.913 (19)
N5–H5B	0.90 (2)	N12–H12B	0.923 (18)
N6–H6A	0.91 (2)		
H1A–O1–H1B	108 (2)	C4–N11–H11A	119.4 (12)
N7–N1–C1	112.95 (11)	C4–N11–H11B	116.1 (13)

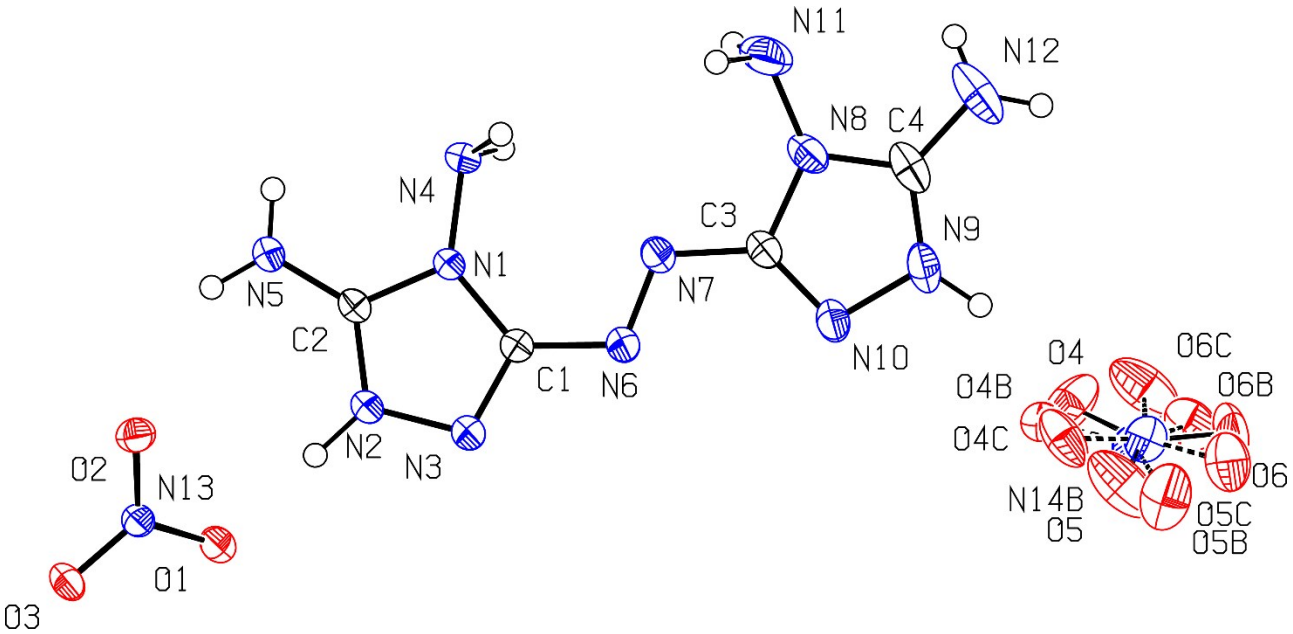
C1–N2–N3	107.13 (10)	H11A–N11–H11B	117.4 (17)
C2–N3–N2	107.73 (11)	N10–N12–H12A	107.0 (12)
C2–N4–C1	105.19 (10)	N10–N12–H12B	110.0 (11)
C2–N4–N6	129.28 (11)	H12A–N12–H12B	108.4 (16)
C1–N4–N6	125.40 (11)	N2–C1–N4	110.27 (11)
C2–N5–H5A	119.4 (14)	N2–C1–N1	130.04 (11)
C2–N5–H5B	116.8 (13)	N4–C1–N1	119.63 (11)
H5A–N5–H5B	116.5 (19)	N3–C2–N5	125.38 (12)
N4–N6–H6A	109.0 (12)	N3–C2–N4	109.68 (11)
N4–N6–H6B	106.9 (13)	N5–C2–N4	124.89 (12)
H6A–N6–H6B	109.0 (17)	N8–C3–N10	110.30 (11)
N1–N7–C3	113.01 (11)	N8–C3–N7	130.78 (12)
C3–N8–N9	107.27 (10)	N10–C3–N7	118.90 (11)
C4–N9–N8	107.52 (10)	N9–C4–N11	126.12 (12)
C4–N10–C3	105.20 (10)	N9–C4–N10	109.67 (11)
C4–N10–N12	129.35 (11)	N11–C4–N10	124.11 (12)
C3–N10–N12	125.44 (11)		
C1–N2–N3–C2	-0.29 (15)	N6–N4–C2–N5	-1.8 (2)
C1–N1–N7–C3	-177.18 (11)	N9–N8–C3–N10	0.05 (15)
C3–N8–N9–C4	-1.01 (14)	N9–N8–C3–N7	178.87 (14)
N3–N2–C1–N4	0.23 (15)	C4–N10–C3–N8	0.90 (15)
N3–N2–C1–N1	177.39 (13)	N12–N10–C3–N8	179.96 (11)
C2–N4–C1–N2	-0.08 (15)	C4–N10–C3–N7	-178.08 (12)
N6–N4–C1–N2	-176.21 (12)	N12–N10–C3–N7	0.98 (19)
C2–N4–C1–N1	-177.58 (12)	N1–N7–C3–N8	-1.4 (2)
N6–N4–C1–N1	6.29 (19)	N1–N7–C3–N10	177.33 (11)
N7–N1–C1–N2	2.9 (2)	N8–N9–C4–N11	-174.95 (12)
N7–N1–C1–N4	179.80 (11)	N8–N9–C4–N10	1.60 (14)
N2–N3–C2–N5	177.84 (13)	C3–N10–C4–N9	-1.53 (14)
N2–N3–C2–N4	0.25 (15)	N12–N10–C4–N9	179.45 (12)
C1–N4–C2–N3	-0.11 (14)	C3–N10–C4–N11	175.09 (12)
N6–N4–C2–N3	175.82 (12)	N12–N10–C4–N11	-3.9 (2)
C1–N4–C2–N5	-177.72 (13)		

Hydrogen-bond geometry (Å, º) for 2b•H_2O

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
O1–H1*A*···N3^{i}	0.90 (3)	1.95 (3)	2.7779 (16)	153 (2)
O1–H1*B*···N9	0.90 (3)	1.94 (3)	2.8413 (16)	171 (2)
N5–H5*A*···N8^{ii}	0.89 (2)	2.13 (2)	2.9852 (17)	160 (2)
N5–H5*B*···N1^{ii}	0.90 (2)	2.60 (2)	3.0252 (16)	110.1 (15)
N5–H5*B*···N6^{ii}	0.90 (2)	2.21 (2)	3.1010 (17)	168.6 (18)
N6–H6*A*···O1^{iii}	0.91 (2)	1.96 (2)	2.8554 (17)	167.6 (18)
N6–H6*B*···N5^{iv}	0.92 (2)	2.38 (2)	3.2448 (18)	157.7 (17)
N11–H11*A*···N2^{v}	0.927 (19)	2.099 (19)	2.9769 (16)	157.6 (16)
N11–H11*B*···N7^{v}	0.88 (2)	2.62 (2)	3.0584 (16)	111.9 (15)
N11–H11*B*···N12^{v}	0.88 (2)	2.20 (2)	3.0749 (18)	172.8 (18)
N12–H12*A*···N11^{vi}	0.913 (19)	2.32 (2)	3.1913 (18)	160.6 (16)
N12–H12*B*···O1^{vii}	0.923 (18)	2.292 (18)	2.9278 (16)	125.6 (15)
N12–H12*B*···N9^{viii}	0.923 (18)	2.530 (18)	3.2619 (17)	136.5 (14)

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) -*x*, *y*-1/2, -*z*-1/2; (iii) -*x*, -*y*+1, -*z*; (iv) -*x*, -*y*, -*z*-1; (v) -*x*+1, *y*+1/2, -*z*+1/2; (vi) -*x*+1, -*y*+1, -*z*+1; (vii) -*x*+1, *y*-1/2, -*z*+1/2; (viii) -*x*+1, -*y*+1, -*z*.–

***Single Crystal XRD data for 4,4',5,5' tetra-amino-3,3'-azo bis-1,2,4-triazolium dinitrate [HTAABTH $(NO_3)_2$]* (3)**



View of the structure of **3**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

One of the two nitrate anions is disordered by rotation in place. It was modeled as disordered over three orientations. The three moieties were restrained to have similar geometries as the other not disordered nitrate anion. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy rates refined to 0.504(3), 0.351(3) and 0.145(2).

$C_4H_{10}N_{12}\cdot 2(NO_3)$	$Z = 2$
$M_r = 350.26$	$F(000) = 360$
Triclinic, $P\bar{1}$	$D_x = 1.776$ Mg m^{-3}
$a = 6.6892$ (2) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 8.6817$ (3) Å	Cell parameters from 9492 reflections
$c = 12.0249$ (5) Å	$\theta = 2.4$–$33.0°$
$\alpha = 80.3377$ (17) °	$\mu = 0.16$ mm^{-1}
$\beta = 75.0338$ (15) °	$T = 150$ K

$\gamma = 77.9914\ (14)\ °$	Block, orange
$V = 655.05\ (4)\ Å^3$	0.22 × 0.20 × 0.15 mm

Data collection

Bruker AXS D8 Quest CMOS diffractometer	29403 measured reflections
Radiation source: fine focus sealed tube X-ray source	4987 independent reflections
Triumph curved graphite crystal monochromator	3554 reflections with $I > 2\sigma(I)$
Detector resolution: 7.4074 pixels mm^{-1}	$R_{int} = 0.046$
ω and phi scans	$\theta_{max} = 33.2°$, $\theta_{min} = 2.8°$
Absorption correction: multi-scan, *SADABS 2016/2, Krause et al., 2015*	$h = -10 \rightarrow 9$
$T_{min} = 0.718$, $T_{max} = 0.747$	$k = -13 \rightarrow 13$
	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.042$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.112$	All H-atom parameters refined
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (\ 0.0496P)^2 + 0.1558P]$ where $P = (F_o^2 + 2F_c^2)/3$
4987 reflections	$(\Delta/\sigma)_{max} < 0.001$
332 parameters	$\Delta\rho_{max} = 0.29\ e\ Å^{-3}$
325 restraints	$\Delta\rho_{min} = -0.26\ e\ Å^{-3}$
Extinction coefficient: n/a	Extinction correction: none

Geometric parameters (Å, º) for 3

N1–C2	1.3517 (13)	N9–H9	0.89 (2)
N1–C1	1.3913 (13)	N10–C3	1.2996 (16)
N1–N4	1.4086 (13)	N11–H11A	0.93 (3)
N2–C2	1.3406 (14)	N11–H11B	0.94 (2)
N2–N3	1.3690 (13)	N12–C4	1.3188 (18)
N2–H2	0.929 (19)	N12–H12A	0.84 (3)
N3–C1	1.3054 (14)	N12–H12B	0.81 (2)
N4–H4A	0.928 (18)	N13–O3	1.2290 (12)
N4–H4B	0.929 (19)	N13–O2	1.2512 (12)
N5–C2	1.3158 (14)	N13–O1	1.2773 (12)

N5–H5A	0.868 (17)	N14–O5	1.221 (7)
N5–H5B	0.855 (18)	N14–O6	1.240 (7)
N6–N7	1.2609 (13)	N14–O4	1.258 (7)
N6–C1	1.3897 (14)	N14B–O6B	1.197 (10)
N7–C3	1.3913 (14)	N14B–O5B	1.245 (11)
N8–C4	1.3435 (17)	N14B–O4B	1.248 (10)
N8–C3	1.3797 (15)	N14C–O6C	1.223 (14)
N8–N11	1.3996 (17)	N14C–O5C	1.255 (14)
N9–C4	1.3260 (19)	N14C–O4C	1.262 (14)
N9–N10	1.3771 (14)		
C2–N1–C1	106.19 (9)	C4–N12–H12B	114.8 (18)
C2–N1–N4	120.56 (9)	H12A–N12–H12B	123 (3)
C1–N1–N4	133.07 (9)	O3–N13–O2	122.32 (10)
C2–N2–N3	111.70 (9)	O3–N13–O1	119.31 (9)
C2–N2–H2	124.5 (12)	O2–N13–O1	118.37 (9)
N3–N2–H2	123.0 (12)	O5–N14–O6	121.7 (7)
C1–N3–N2	104.58 (9)	O5–N14–O4	118.8 (7)
N1–N4–H4A	107.4 (11)	O6–N14–O4	119.5 (6)
N1–N4–H4B	107.8 (11)	O6B–N14B–O5B	118.4 (10)
H4A–N4–H4B	107.6 (15)	O6B–N14B–O4B	121.6 (10)
C2–N5–H5A	119.3 (11)	O5B–N14B–O4B	119.4 (9)
C2–N5–H5B	117.7 (11)	O6C–N14C–O5C	122.4 (18)
H5A–N5–H5B	122.6 (15)	O6C–N14C–O4C	114.3 (16)
N7–N6–C1	111.84 (9)	O5C–N14C–O4C	119.2 (16)
N6–N7–C3	114.13 (9)	N3–C1–N6	119.56 (9)
C4–N8–C3	106.69 (11)	N3–C1–N1	111.23 (9)
C4–N8–N11	120.93 (11)	N6–C1–N1	129.19 (9)
C3–N8–N11	132.29 (11)	N5–C2–N2	128.23 (10)
C4–N9–N10	112.17 (11)	N5–C2–N1	125.49 (10)
C4–N9–H9	131.8 (14)	N2–C2–N1	106.27 (9)
N10–N9–H9	115.9 (14)	N10–C3–N8	111.51 (10)
C3–N10–N9	103.66 (10)	N10–C3–N7	131.08 (10)
N8–N11–H11A	104.0 (17)	N8–C3–N7	117.41 (10)
N8–N11–H11B	105.9 (13)	N12–C4–N9	129.46 (16)
H11A–N11–H11B	108 (2)	N12–C4–N8	124.58 (16)

C4–N12–H12A	121.3 (19)	N9–C4–N8	105.96 (10)
C2–N2–N3–C1	1.30 (12)	N4–N1–C2–N2	177.61 (9)
C1–N6–N7–C3	-177.47 (9)	N9–N10–C3–N8	0.32 (13)
C4–N9–N10–C3	0.35 (14)	N9–N10–C3–N7	179.26 (12)
N2–N3–C1–N6	-178.73 (9)	C4–N8–C3–N10	-0.86 (14)
N2–N3–C1–N1	-0.05 (12)	N11–N8–C3–N10	-177.47 (15)
N7–N6–C1–N3	-175.39 (10)	C4–N8–C3–N7	-179.96 (10)
N7–N6–C1–N1	6.19 (16)	N11–N8–C3–N7	3.4 (2)
C2–N1–C1–N3	-1.17 (12)	N6–N7–C3–N10	3.16 (18)
N4–N1–C1–N3	-176.13 (11)	N6–N7–C3–N8	-177.95 (10)
C2–N1–C1–N6	177.36 (11)	N10–N9–C4–N12	179.15 (14)
N4–N1–C1–N6	2.4 (2)	N10–N9–C4–N8	-0.87 (15)
N3–N2–C2–N5	179.12 (11)	C3–N8–C4–N12	-179.01 (13)
N3–N2–C2–N1	-2.03 (12)	N11–N8–C4–N12	-1.9 (2)
C1–N1–C2–N5	-179.23 (10)	C3–N8–C4–N9	1.01 (14)
N4–N1–C2–N5	-3.50 (16)	N11–N8–C4–N9	178.09 (14)
C1–N1–C2–N2	1.88 (11)		

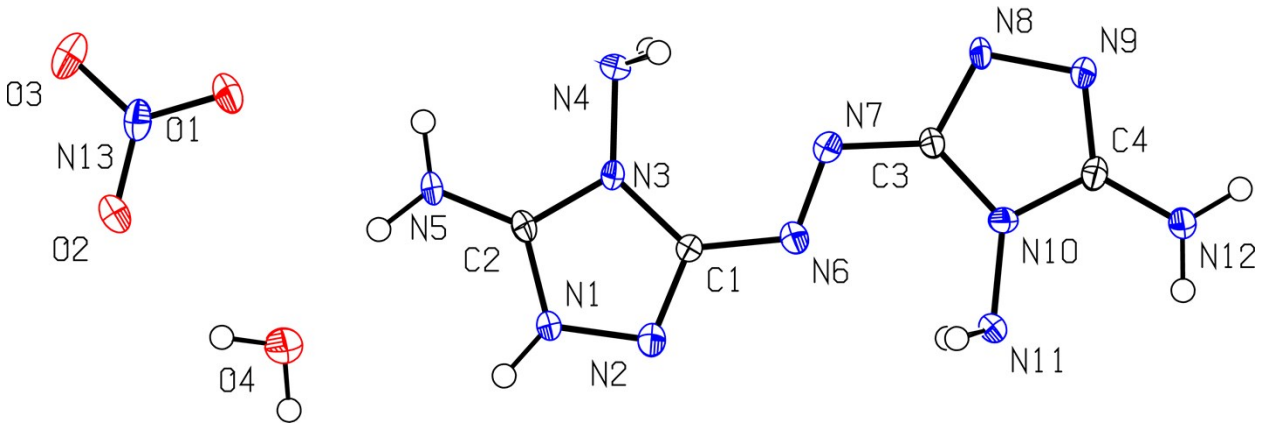
Hydrogen-bond geometry (Å, º) for 3

D–H···*A*	*D*–H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*–H···*A* (°)
N2–H2···N13	0.929 (19)	2.490 (19)	3.3500 (13)	154.1 (15)
N2–H2···O1	0.929 (19)	1.770 (19)	2.6959 (12)	173.9 (17)
N2–H2···O2	0.929 (19)	2.516 (19)	3.1441 (13)	125.1 (14)
N4–H4A···O5^{i}	0.928 (18)	2.651 (18)	3.251 (5)	123.0 (13)
N4–H4A···O6^{ii}	0.928 (18)	2.217 (18)	3.046 (4)	148.3 (14)
N4–H4A···O6B^{ii}	0.928 (18)	2.142 (19)	2.987 (4)	150.9 (15)
N4–H4A···O4C^{i}	0.928 (18)	2.351 (19)	2.958 (8)	122.8 (14)
N4–H4A···O6C^{ii}	0.928 (18)	2.31 (2)	3.172 (13)	155.1 (15)
N4–H4B···O2^{iii}	0.929 (19)	2.192 (19)	3.1168 (13)	173.1 (16)
N5–H5A···O2	0.868 (17)	2.431 (17)	3.1088 (13)	135.3 (13)
N5–H5A···O3^{iv}	0.868 (17)	2.330 (16)	3.0824 (13)	145.2 (14)
N5–H5B···N13^{v}	0.855 (18)	2.712 (17)	3.4365 (14)	143.5 (14)
N5–H5B···O1^{v}	0.855 (18)	2.039 (18)	2.8851 (13)	170.1 (16)
N9–H9···O4	0.89 (2)	1.93 (2)	2.771 (3)	157.4 (19)

N9–H9···O6^{vi}	0.89 (2)	2.42 (2)	2.894 (3)	113.8 (16)
N9–H9···O4B	0.89 (2)	1.72 (2)	2.532 (4)	151 (2)
N9–H9···O4C	0.89 (2)	2.18 (3)	2.948 (16)	144.5 (19)
N9–H9···O5C^{vi}	0.89 (2)	2.43 (2)	2.893 (10)	112.6 (17)
N9–H9···O6C	0.89 (2)	2.58 (3)	3.442 (19)	163.7 (18)
N11–H11A···O4^{ii}	0.93 (3)	1.93 (3)	2.774 (4)	150 (2)
N11–H11A···O4B^{ii}	0.93 (3)	2.64 (3)	3.454 (10)	146 (2)
N11–H11A···O6B^{ii}	0.93 (3)	2.55 (3)	3.436 (6)	159 (2)
N11–H11A···O6C^{ii}	0.93 (3)	2.18 (3)	3.041 (11)	153 (2)
N11–H11B···N13^{iii}	0.94 (2)	2.64 (2)	3.5344 (18)	160.3 (17)
N11–H11B···O2^{iii}	0.94 (2)	2.19 (2)	3.1194 (17)	168.9 (18)
N11–H11B···O3^{iii}	0.94 (2)	2.45 (2)	3.1794 (18)	134.4 (17)
N12–H12A···O5^{v}	0.84 (3)	2.46 (3)	2.958 (5)	119 (2)
N12–H12A···O6^{vi}	0.84 (3)	2.16 (3)	2.781 (5)	131 (2)
N12–H12A···O5B^{vi}	0.84 (3)	2.29 (3)	3.101 (6)	162 (2)
N12–H12A···O5C^{vi}	0.84 (3)	1.78 (3)	2.518 (10)	144 (3)
N12–H12B···O4B^{v}	0.81 (2)	2.34 (2)	2.754 (4)	112 (2)

Symmetry code(s): (i) *x*, *y*+1, *z*; (ii) -*x*+2, -*y*+1, -*z*+1; (iii) -*x*+1, -*y*+2, -*z*+2; (iv) -*x*, -*y*+3, -*z*+2; (v) *x*+1, *y*, *z*; (vi) -*x*+2, -*y*, -*z*+1.

Single Crystal XRD data for 4,4',5,5' tetra-amino-3,3'-azo bis-1,2,4-triazolium nitrate monohydrate [TAABTH NO_3•H_2O] (4•H_2O)



View of the structure of **4•H_2O**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

The crystal under investigation was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell_Now, with the two components being related by a 180° rotation around the reciprocal axis (1 0 -1). The two components were integrated using Saint and corrected for absorption using twinabs, resulting in the following statistics:

3051 data (1265 unique) involve domain 1 only, mean I/sigma 41.9

3063 data (1243 unique) involve domain 2 only, mean I/sigma 27.5

10648 data (3199 unique) involve 2 domains, mean I/sigma 33.9

The exact twin matrix identified by the integration program was found to be:

0.31844 -0.00008 -0.68292

-0.00022 -1.00000 0.00027

-1.31582 0.00004 -0.31844

The structure was solved using direct methods with only the non-overlapping reflections of component 1. The structure was refined using the hklf 5 routine with all reflections of component 1 (including the overlapping ones), resulting in a BASF value of 0.297(3). The R_{int} value given is for all reflections and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions (TWINABS (Sheldrick, 2012)).

Crystal data

$C_4H_9N_{12}\cdot NO_3\cdot H_2O$	$F(000) = 632$
$M_r = 305.26$	$D_x = 1.752$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.308$ (3) Å	Cell parameters from 7494 reflections
$b = 16.635$ (7) Å	$\theta = 2.5–30.6°$
$c = 9.625$ (4) Å	$\mu = 0.15$ mm^{-1}
$\beta = 98.404$ (14)°	$T = 150$ K
$V = 1157.5$ (8) Å^3	Plate, orange
$Z = 4$	0.33 × 0.28 × 0.11 mm

Data collection

Bruker AXS D8 Quest CMOS diffractometer	16546 measured reflections
Radiation source: fine focus sealed tube X-ray source	2799 independent reflections
Triumph curved graphite crystal monochromator	2363 reflections with $I > 2\sigma(I)$
Detector resolution: 10.4167 pixels mm^{-1}	$R_{int} = 0.123$
ω and phi scans	$\theta_{max} = 28.3°$, $\theta_{min} = 2.5°$
Absorption correction: multi-scan, TWINABS 2012/1, Krause et al., 2015	$h = -9\rightarrow9$
$T_{min} = 0.290$, $T_{max} = 0.433$	$k = 0\rightarrow22$
	$l = 0\rightarrow12$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.083$	Hydrogen site location: mixed
$wR(F^2) = 0.237$	H atoms treated by a mixture of indep. and constr. refinement
$S = 1.02$	$w = 1/[\sigma^2(F_o^2) + (0.1563P)^2 + 1.613P]$ where $P = (F_o^2 + 2F_c^2)/3$
2799 reflections	$(\Delta/\sigma)_{max} < 0.001$
210 parameters	$\Delta\rho_{max} = 0.79$ e Å^{-3}
9 restraints	$\Delta\rho_{min} = -0.52$ e Å^{-3}
Extinction coefficient: 0.12 (2)	Extinction correction: *SHELXL2018*/3 (Sheldrick, 2018), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

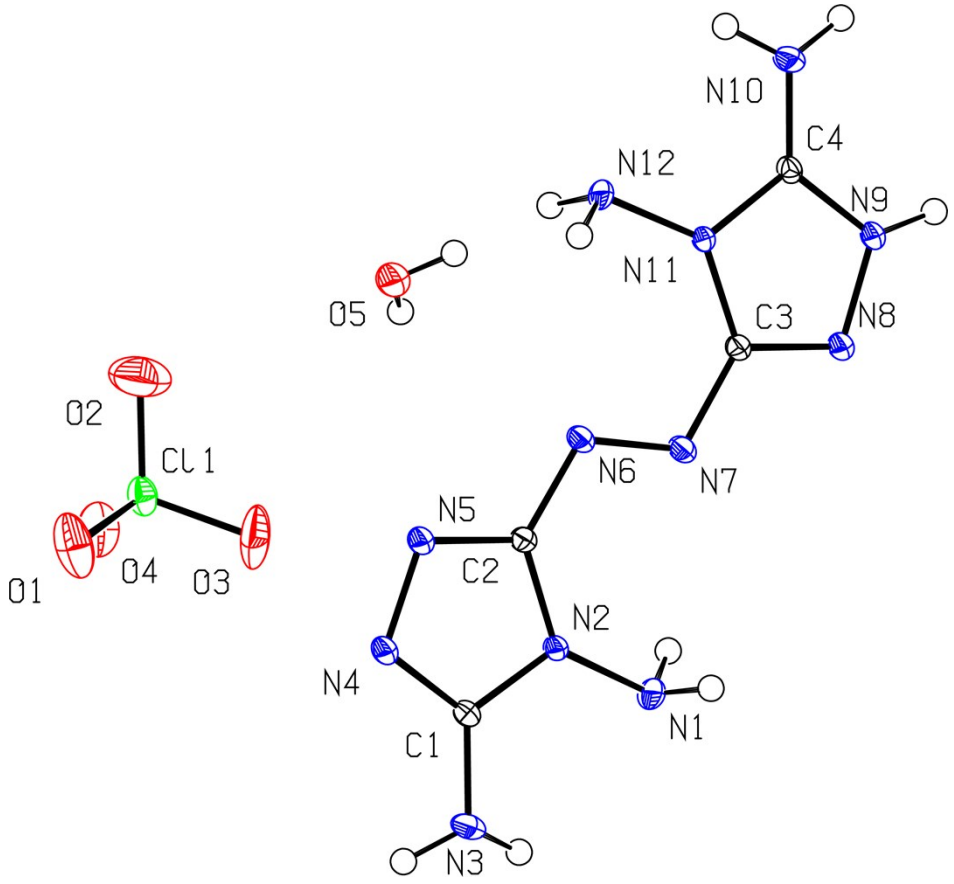
Geometric parameters (Å, º) for 4•H_2O

C1–N2	1.298 (5)	N4–H4B	0.877 (19)

C1–N6	1.384 (4)	N5–H5A	0.8800
C1–N3	1.389 (4)	N5–H5B	0.8800
C2–N5	1.302 (5)	N6–N7	1.267 (4)
C2–N1	1.341 (5)	N8–N9	1.372 (4)
C2–N3	1.344 (4)	N10–N11	1.419 (4)
C3–N8	1.337 (5)	N11–H11A	0.873 (19)
C3–N7	1.368 (4)	N11–H11B	0.877 (19)
C3–N10	1.376 (4)	N12–H12A	0.8800
C4–N12	1.323 (4)	N12–H12B	0.8800
C4–N9	1.327 (4)	N13–O1	1.237 (4)
C4–N10	1.343 (4)	N13–O3	1.251 (5)
N1–N2	1.361 (4)	N13–O2	1.268 (5)
N1–H8	0.8800	O4–H4OA	0.864 (19)
N3–N4	1.413 (4)	O4–H4OB	0.837 (19)
N4–H4A	0.869 (19)		
N2–C1–N6	118.0 (3)	H4A–N4–H4B	103 (3)
N2–C1–N3	111.3 (3)	C2–N5–H5A	120.0
N6–C1–N3	130.7 (3)	C2–N5–H5B	120.0
N5–C2–N1	126.5 (3)	H5A–N5–H5B	120.0
N5–C2–N3	127.6 (3)	N7–N6–C1	115.9 (3)
N1–C2–N3	105.9 (3)	N6–N7–C3	112.4 (3)
N8–C3–N7	120.7 (3)	C3–N8–N9	107.7 (3)
N8–C3–N10	108.8 (3)	C4–N9–N8	106.9 (3)
N7–C3–N10	130.4 (3)	C4–N10–C3	105.6 (3)
N12–C4–N9	125.7 (3)	C4–N10–N11	122.6 (3)
N12–C4–N10	123.4 (3)	C3–N10–N11	131.6 (3)
N9–C4–N10	110.9 (3)	N10–N11–H11A	101 (3)
C2–N1–N2	112.0 (3)	N10–N11–H11B	104 (3)
C2–N1–H8	124.0	H11A–N11–H11B	102 (4)
N2–N1–H8	124.0	C4–N12–H12A	120.0
C1–N2–N1	104.5 (3)	C4–N12–H12B	120.0
C2–N3–C1	106.3 (3)	H12A–N12–H12B	120.0
C2–N3–N4	121.5 (3)	O1–N13–O3	121.1 (4)
C1–N3–N4	132.2 (3)	O1–N13–O2	119.5 (3)
N3–N4–H4A	105 (4)	O3–N13–O2	119.4 (4)

N3–N4–H4B	104 (4)	H4OA–O4–H4OB	104 (3)
N5–C2–N1–N2	179.6 (4)	N8–C3–N7–N6	177.0 (4)
N3–C2–N1–N2	-1.3 (5)	N10–C3–N7–N6	-1.3 (6)
N6–C1–N2–N1	178.7 (3)	N7–C3–N8–N9	179.5 (3)
N3–C1–N2–N1	-1.5 (5)	N10–C3–N8–N9	-1.9 (4)
C2–N1–N2–C1	1.7 (5)	N12–C4–N9–N8	177.4 (4)
N5–C2–N3–C1	179.4 (4)	N10–C4–N9–N8	-0.7 (4)
N1–C2–N3–C1	0.3 (4)	C3–N8–N9–C4	1.6 (4)
N5–C2–N3–N4	-0.5 (7)	N12–C4–N10–C3	-178.6 (4)
N1–C2–N3–N4	-179.7 (4)	N9–C4–N10–C3	-0.4 (4)
N2–C1–N3–C2	0.8 (5)	N12–C4–N10–N11	6.6 (6)
N6–C1–N3–C2	-179.4 (4)	N9–C4–N10–N11	-175.2 (3)
N2–C1–N3–N4	-179.2 (4)	N8–C3–N10–C4	1.4 (4)
N6–C1–N3–N4	0.5 (8)	N7–C3–N10–C4	179.8 (4)
N2–C1–N6–N7	-178.0 (4)	N8–C3–N10–N11	175.5 (4)
N3–C1–N6–N7	2.3 (6)	N7–C3–N10–N11	-6.0 (7)
C1–N6–N7–C3	-179.0 (3)		

Single Crystal XRD data for 4,4',5,5' tetra-amino-3,3'-azo bis-1,2,4-triazolium perchlorate monohydrate (TAABTH ClO_4•H_2O) (5•H_2O)



View of the structure of **5•H_2O**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Crystal data

$C_4H_9N_{12}·ClO_4·H_2O$	$F(000)$ = 704
M_r = 342.70	D_x = 1.748 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 7.6478 (4) Å	Cell parameters from 9515 reflections
b = 18.7539 (10) Å	θ = 2.8–33.2°
c = 9.4649 (5) Å	μ = 0.35 mm^{-1}
β = 106.3617 (16)°	T = 150 K
V = 1302.54 (12) Å^3	Plate, orange
Z = 4	0.35 × 0.33 × 0.16 mm

Data collection

Bruker AXS D8 Quest CMOS diffractometer	40210 measured reflections
Radiation source: fine focus sealed tube X-ray source	4960 independent reflections
Triumph curved graphite crystal monochromator	4518 reflections with $I > 2\sigma(I)$
Detector resolution: 10.4167 pixels mm^{-1}	$R_{int} = 0.031$
ω and phi scans	$\theta_{max} = 33.2°$, $\theta_{min} = 2.5°$
Absorption correction: multi-scan, *SADABS 2016/2, Krause et al., 2015*	$h = -10 \rightarrow 11$
$T_{min} = 0.698$, $T_{max} = 0.747$	$k = -28 \rightarrow 28$
	$l = -11 \rightarrow 14$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.032$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.088$	All H-atom parameters refined
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.5919P]$ where $P = (F_o^2 + 2F_c^2)/3$
4960 reflections	$(\Delta/\sigma)_{max} = 0.001$
243 parameters	$\Delta\rho_{max} = 0.54$ e $Å^{-3}$
0 restraints	$\Delta\rho_{min} = -0.64$ e $Å^{-3}$

Geometric parameters (Å, º) for 5•H_2O

Cl1–O2	1.4253 (10)	N3–H3A	0.884 (17)
Cl1–O3	1.4321 (8)	N3–H3B	0.872 (17)
Cl1–O4	1.4357 (8)	C4–N10	1.3154 (10)
Cl1–O1	1.4445 (8)	C4–N9	1.3431 (10)
N1–N2	1.4060 (10)	C4–N11	1.3558 (10)
N1–H1A	0.906 (17)	N4–N5	1.3741 (10)
N1–H1B	0.881 (16)	O5–H5A	0.83 (2)
C1–N4	1.3365 (10)	O5–H5B	0.83 (2)
C1–N3	1.3481 (11)	N6–N7	1.2719 (10)
C1–N2	1.3535 (10)	N8–N9	1.3687 (10)
C2–N5	1.3167 (10)	N9–H9	0.91 (2)
C2–N6	1.3797 (10)	N10–H10A	0.895 (17)
C2–N2	1.3873 (10)	N10–H10B	0.904 (17)
C3–N8	1.3096 (10)	N11–N12	1.4038 (9)

C3–N7	1.3859 (10)	N12–H12A	0.880 (16)
C3–N11	1.3923 (10)	N12–H12B	0.893 (16)
O2–Cl1–O3	110.51 (7)	H3A–N3–H3B	117.8 (16)
O2–Cl1–O4	109.82 (7)	N10–C4–N9	127.82 (7)
O3–Cl1–O4	109.86 (6)	N10–C4–N11	125.62 (7)
O2–Cl1–O1	109.55 (7)	N9–C4–N11	106.55 (7)
O3–Cl1–O1	108.38 (6)	C1–N4–N5	107.41 (6)
O4–Cl1–O1	108.68 (5)	C2–N5–N4	107.63 (7)
N2–N1–H1A	109.0 (10)	H5A–O5–H5B	109 (2)
N2–N1–H1B	107.7 (10)	N7–N6–C2	114.19 (7)
H1A–N1–H1B	105.4 (14)	N6–N7–C3	113.31 (7)
N4–C1–N3	126.92 (8)	C3–N8–N9	105.25 (7)
N4–C1–N2	110.15 (7)	C4–N9–N8	111.15 (7)
N3–C1–N2	122.80 (8)	C4–N9–H9	125.4 (12)
N5–C2–N6	119.70 (7)	N8–N9–H9	121.1 (12)
N5–C2–N2	109.91 (7)	C4–N10–H10A	120.5 (11)
N6–C2–N2	130.39 (7)	C4–N10–H10B	117.7 (11)
C1–N2–C2	104.89 (7)	H10A–N10–H10B	119.5 (15)
C1–N2–N1	121.16 (7)	C4–N11–C3	106.21 (6)
C2–N2–N1	133.86 (7)	C4–N11–N12	120.50 (7)
N8–C3–N7	118.94 (7)	C3–N11–N12	132.94 (7)
N8–C3–N11	110.75 (7)	N11–N12–H12A	107.5 (10)
N7–C3–N11	130.30 (7)	N11–N12–H12B	107.7 (10)
C1–N3–H3A	114.0 (11)	H12A–N12–H12B	106.7 (15)
C1–N3–H3B	117.2 (11)		
N4–C1–N2–C2	-0.14 (9)	N8–C3–N7–N6	-175.41 (7)
N3–C1–N2–C2	-176.29 (8)	N11–C3–N7–N6	5.15 (12)
N4–C1–N2–N1	-177.19 (7)	N7–C3–N8–N9	179.83 (7)
N3–C1–N2–N1	6.65 (12)	N11–C3–N8–N9	-0.62 (9)
N5–C2–N2–C1	-0.47 (9)	N10–C4–N9–N8	-177.97 (8)
N6–C2–N2–C1	179.59 (8)	N11–C4–N9–N8	2.63 (9)
N5–C2–N2–N1	176.03 (8)	C3–N8–N9–C4	-1.25 (9)
N6–C2–N2–N1	-3.90 (15)	N10–C4–N11–C3	177.73 (8)
N3–C1–N4–N5	176.62 (8)	N9–C4–N11–C3	-2.85 (9)

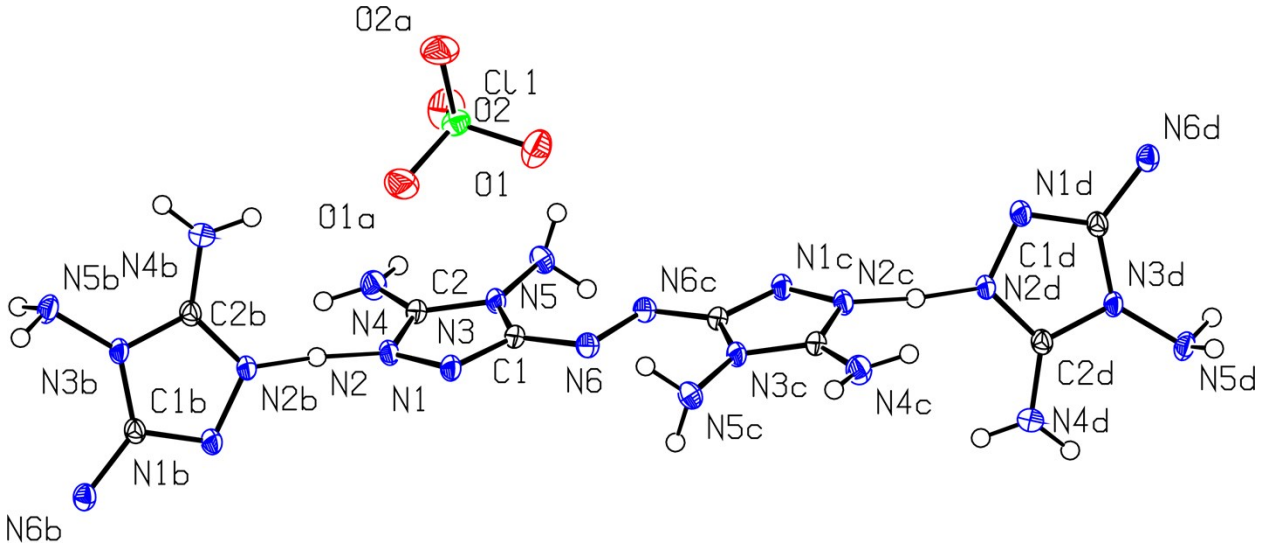
N2–C1–N4–N5	0.66 (9)	N10–C4–N11–N12	3.63 (12)
N6–C2–N5–N4	-179.18 (7)	N9–C4–N11–N12	-176.95 (7)
N2–C2–N5–N4	0.88 (9)	N8–C3–N11–C4	2.21 (9)
C1–N4–N5–C2	-0.95 (9)	N7–C3–N11–C4	-178.31 (8)
N5–C2–N6–N7	174.26 (8)	N8–C3–N11–N12	175.25 (8)
N2–C2–N6–N7	-5.81 (13)	N7–C3–N11–N12	-5.26 (14)
C2–N6–N7–C3	179.78 (7)		

Hydrogen-bond geometry (Å, º) for 5•H_2O

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
N1–H1*A*···O2^{i}	0.906 (17)	2.450 (16)	3.0165 (14)	120.8 (13)
N1–H1*A*···O4^{ii}	0.906 (17)	2.411 (16)	3.0403 (13)	126.6 (13)
N1–H1*B*···N5^{iii}	0.881 (16)	2.277 (16)	3.1151 (11)	159.0 (14)
N3–H3*B*···O3^{iv}	0.872 (17)	2.124 (17)	2.9637 (12)	161.4 (16)
O5–H5*A*···N3^{iii}	0.83 (2)	2.30 (2)	3.0768 (12)	154.8 (19)
O5–H5*B*···Cl1^{v}	0.83 (2)	2.82 (2)	3.6062 (8)	159 (2)
O5–H5*B*···O4^{v}	0.83 (2)	2.63 (2)	3.2144 (12)	128.7 (19)
O5–H5*B*···O1^{v}	0.83 (2)	2.00 (2)	2.8277 (12)	172 (2)
N9–H9···N4^{vi}	0.91 (2)	1.83 (2)	2.7416 (10)	175.2 (18)
N10–H10*A*···O5^{v}	0.895 (17)	1.978 (17)	2.8365 (11)	160.2 (16)
N10–H10*B*···O5^{vii}	0.904 (17)	2.018 (17)	2.8576 (11)	153.9 (15)
N12–H12*A*···N8^{iv}	0.880 (16)	2.285 (16)	3.0957 (10)	153.2 (14)
N12–H12*B*···O2^{viii}	0.893 (16)	2.584 (16)	3.2013 (15)	126.9 (13)
N12–H12*B*···O1^{v}	0.893 (16)	2.470 (16)	3.0487 (11)	122.9 (13)

Symmetry codes: (i) -*x*+1, *y*-1/2, -*z*+1/2; (ii) *x*+1, -*y*+1/2, *z*+1/2; (iii) *x*, -*y*+1/2, *z*-1/2; (iv) *x*, -*y*+1/2, *z*+1/2; (v) *x*+1, *y*, *z*; (vi) *x*+1, -*y*+1/2, *z*-1/2; (vii) -*x*+2, -*y*+1, -*z*+1; (viii) -*x*+1, -*y*+1, -*z*+1.

***Single Crystal XRD data for 4,4',5,5' tetra-amino-3,3'-azo bis-1,2,4-triazolium perchlorate (TAABTH ClO_4)* (5)**



View of the structure of **5**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (*a*) 1 − *x*, *y*, 1/2 − *z*; (*b*) − *x*, *y*, 1/2 − *z*; (*c*) 1 − *x*, −*y*, −*z*; (*d*) 1 + *x*, −*y*, −1/2 + *z*.

Crystal data

$C_4H_9N_{12}\cdot ClO_4$	$F(000) = 332$
$M_r = 324.68$	$D_x = 1.821$ Mg m^{-3}
Monoclinic, *P*2/*c*	Cu *K*α radiation, λ = 1.54178 Å
a = 7.4095 (6) Å	Cell parameters from 2733 reflections
b = 8.6931 (9) Å	θ = 5.1–79.2°
c = 9.5541 (7) Å	μ = 3.34 mm^{-1}
β = 105.797 (5)°	*T* = 150 K
V = 592.15 (9) Å^3	Needle, yellow
Z = 2	

Data collection

Bruker AXS D8 Quest diffractometer with PhotonII CPAD detector	4375 measured reflections
Radiation source: I-mu-S microsource X-ray tube	1237 independent reflections
Laterally graded multilayer (Goebel) mirror monochromator	1076 reflections with $I > 2\sigma(I)$
Detector resolution: 7.4074 pixels mm^{-1}	$R_{int} = 0.062$
ω and phi scans	$\theta_{max} = 80.9°$, $\theta_{min} = 5.1°$

Absorption correction: multi-scan, *SADABS 2016/2, Krause et al., 2015*	h = -9→8
T_{min} = 0.398, T_{max} = 0.754	k = -10→11
	l = -9→11

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.053	Hydrogen site location: difference Fourier map
$wR(F^2)$ = 0.161	All H-atom parameters refined
S = 1.09	$w = 1/[\sigma^2(F_o^2) + (0.0886P)^2 + 0.7436P]$ where $P = (F_o^2 + 2F_c^2)/3$
1237 reflections	$(\Delta/\sigma)_{max} < 0.001$
114 parameters	$\Delta\rho_{max}$ = 0.42 e Å^{-3}
6 restraints	$\Delta\rho_{min}$ = -0.54 e Å^{-3}

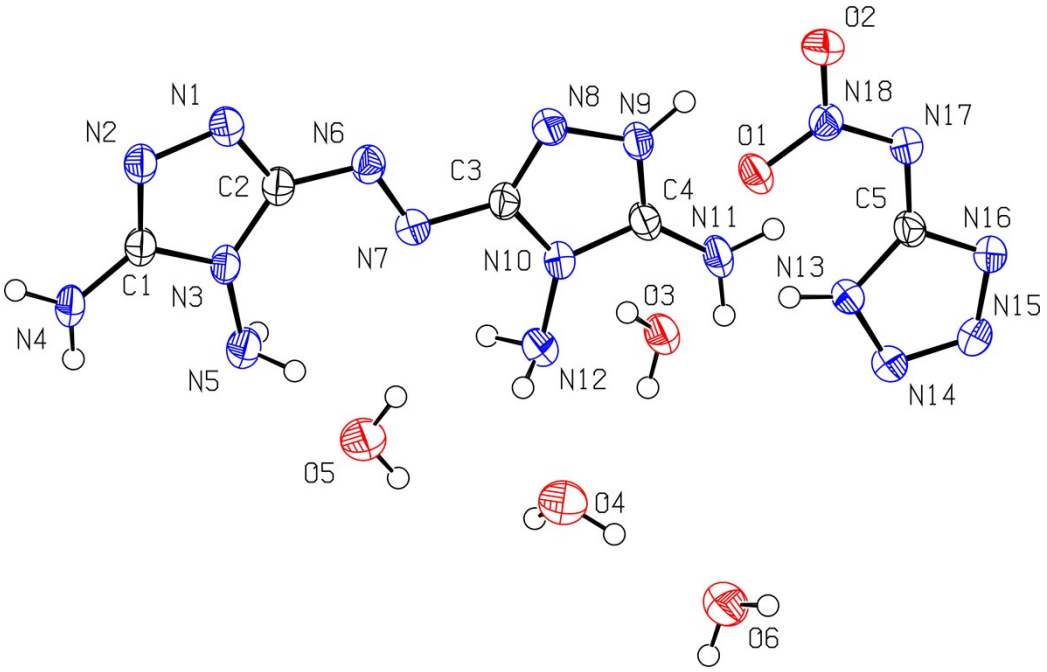
Geometric parameters (Å, º) for 5

Cl1–O2^{i}	1.431 (2)	N2–H2	1.288 (6)
Cl1–O2	1.431 (2)	C2–N4	1.329 (4)
Cl1–O1	1.432 (2)	C2–N3	1.347 (3)
Cl1–O1^{i}	1.432 (2)	N5–N3	1.406 (3)
C1–N1	1.306 (3)	N5–H5A	0.90 (3)
C1–N6	1.385 (4)	N5–H5B	0.89 (3)
C1–N3	1.388 (3)	N4–H4A	0.88 (3)
N1–N2	1.368 (3)	N4–H4B	0.89 (2)
N2–C2	1.336 (3)	N6–N6^{ii}	1.265 (4)
O2^{i}–Cl1–O2	109.6 (2)	N4–C2–N2	126.7 (2)
O2^{i}–Cl1–O1	110.09 (15)	N4–C2–N3	125.1 (2)
O2–Cl1–O1	108.99 (14)	N2–C2–N3	108.2 (2)
O2^{i}–Cl1–O1^{i}	108.99 (14)	N3–N5–H5A	108 (3)
O2–Cl1–O1^{i}	110.09 (15)	N3–N5–H5B	109 (3)
O1–Cl1–O1^{i}	109.0 (2)	H5A–N5–H5B	108 (4)
N1–C1–N6	118.6 (2)	C2–N4–H4A	118 (3)
N1–C1–N3	110.6 (2)	C2–N4–H4B	120 (3)
N6–C1–N3	130.8 (2)	H4A–N4–H4B	119 (4)
C1–N1–N2	106.0 (2)	C2–N3–C1	105.5 (2)

C2–N2–N1	109.6 (2)	C2–N3–N5	121.6 (2)
C2–N2–H2	129 (4)	C1–N3–N5	132.9 (2)
N1–N2–H2	118 (3)	N6^{ii}–N6–C1	113.3 (3)
N6–C1–N1–N2	-178.2 (2)	N2–C2–N3–N5	179.6 (2)
N3–C1–N1–N2	0.0 (3)	N1–C1–N3–C2	0.5 (3)
C1–N1–N2–C2	-0.5 (3)	N6–C1–N3–C2	178.4 (3)
N1–N2–C2–N4	-178.9 (3)	N1–C1–N3–N5	-179.9 (3)
N1–N2–C2–N3	0.8 (3)	N6–C1–N3–N5	-2.0 (5)
N4–C2–N3–C1	178.9 (3)	N1–C1–N6–N6^{ii}	-177.2 (3)
N2–C2–N3–C1	-0.8 (3)	N3–C1–N6–N6^{ii}	5.0 (5)
N4–C2–N3–N5	-0.7 (4)		

Symmetry codes: (i) -*x*+1, *y*, -*z*+1/2; (ii) -*x*+1, -*y*, -*z*.

***Single Crystal XRD data for 4,4',5,5' tetra-amino-3,3'-azo bis-1,2,4-triazolium 5-nitrimino-1,2,3,4-tetrazolate tetrahydrate (TAABTH $CHN_6O_2 \cdot 4H_2O$)* (6•$4H_2O$)**



View of the structure of **6•4H_2O**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Crystal data

$C_4H_9N_{12} \cdot CHN_6O_2 \cdot 4(H_2O)$	$F(000) = 888$
$M_r = 426.37$	$D_x = 1.622$ Mg m^{-3}
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$a = 6.9012$ (4) Å	Cell parameters from 6846 reflections
$b = 15.0471$ (8) Å	$\theta = 2.6–79.9°$
$c = 16.8109$ (10) Å	$\mu = 1.24$ mm^{-1}
$\beta = 90.012$ (4)°	$T = 150$ K
$V = 1745.69$ (17) Å^3	Needle, red
$Z = 4$	0.55 × 0.05 × 0.03 mm

Data collection

Bruker AXS D8 Quest diffractometer with PhotonII CPAD detector	13925 measured reflections
Radiation source: I-mu-S microsource X-ray tube	3710 independent reflections
Laterally graded multilayer (Goebel) mirror monochromator	3087 reflections with $I > 2\sigma(I)$

Detector resolution: 7.4074 pixels mm^{-1}	R_{int} = 0.076
ω and phi scans	θ_{max} = 80.3°, θ_{min} = 2.6°
Absorption correction: multi-scan, *SADABS 2016/2, Krause et al., 2015*	h = -5→8
T_{min} = 0.625, T_{max} = 0.754	k = -19→18
	l = -21→21

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.052	Hydrogen site location: mixed
$wR(F^2)$ = 0.144	H atoms treated by a mixture of indep. and constr. refinement
S = 1.09	$w = 1/[\sigma^2(F_o^2) + (0.0582P)^2 + 0.7079P]$ where $P = (F_o^2 + 2F_c^2)/3$
3710 reflections	$(\Delta/\sigma)_{max} < 0.001$
311 parameters	$\Delta\rho_{max}$ = 0.40 e $Å^{-3}$
20 restraints	$\Delta\rho_{min}$ = -0.29 e $Å^{-3}$

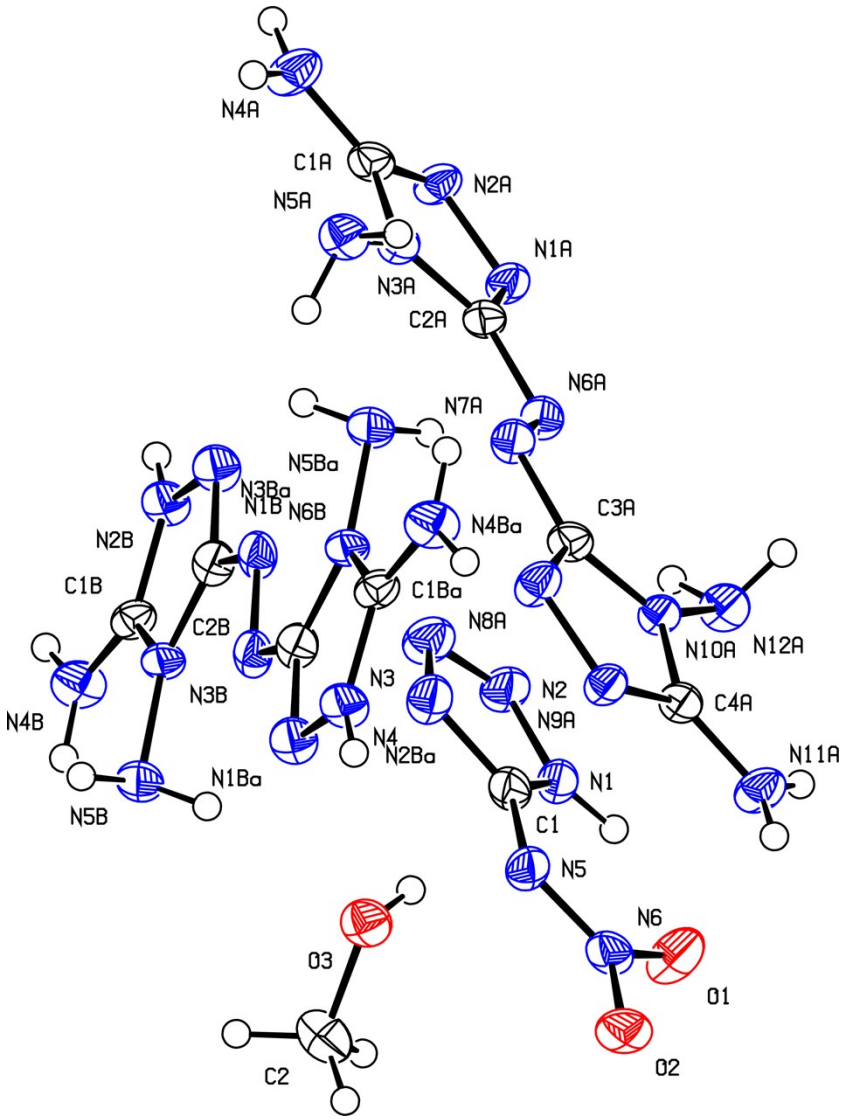
Geometric parameters (Å, º) for 6•4H2O

C1–N4	1.324 (4)	N8–N9	1.385 (4)
C1–N2	1.329 (4)	N9–H9	0.8800
C1–N3	1.361 (4)	N10–N12	1.389 (4)
C2–N1	1.325 (4)	N11–H11A	0.885 (19)
C2–N6	1.364 (4)	N11–H11B	0.886 (19)
C2–N3	1.389 (4)	N12–H12A	0.878 (19)
C3–N8	1.301 (4)	N12–H12B	0.887 (19)
C3–N10	1.372 (4)	N13–N14	1.348 (4)
C3–N7	1.394 (4)	N13–H13	0.8800
C4–N11	1.314 (4)	N14–N15	1.296 (4)
C4–N9	1.327 (5)	N15–N16	1.340 (4)
C4–N10	1.352 (4)	N17–N18	1.324 (4)
C5–N16	1.338 (4)	N18–O2	1.237 (4)
C5–N13	1.348 (4)	N18–O1	1.258 (4)
C5–N17	1.361 (4)	O3–H3O1	0.826 (19)
N1–N2	1.360 (4)	O3–H3O2	0.824 (18)
N3–N5	1.413 (4)	O4–H4O1	0.867 (19)
N4–H4A	0.887 (19)	O4–H4O2	0.862 (19)

N4–H4B	0.885 (19)	O5–H5O1	0.838 (19)
N5–H5A	0.873 (19)	O5–H5O2	0.844 (19)
N5–H5B	0.875 (19)	O6–H6O1	0.815 (19)
N6–N7	1.281 (4)	O6–H6O2	0.843 (19)
N4–C1–N2	126.2 (3)	C3–N8–N9	103.3 (3)
N4–C1–N3	123.4 (3)	C4–N9–N8	112.4 (3)
N2–C1–N3	110.4 (3)	C4–N9–H9	123.8
N1–C2–N6	119.5 (3)	N8–N9–H9	123.8
N1–C2–N3	109.0 (2)	C4–N10–C3	107.0 (3)
N6–C2–N3	131.5 (3)	C4–N10–N12	122.7 (3)
N8–C3–N10	111.8 (3)	C3–N10–N12	130.2 (3)
N8–C3–N7	129.8 (3)	C4–N11–H11A	122 (3)
N10–C3–N7	118.4 (3)	C4–N11–H11B	125 (3)
N11–C4–N9	128.6 (3)	H11A–N11–H11B	111 (4)
N11–C4–N10	126.0 (3)	N10–N12–H12A	101 (3)
N9–C4–N10	105.4 (3)	N10–N12–H12B	112 (3)
N16–C5–N13	106.9 (3)	H12A–N12–H12B	101 (4)
N16–C5–N17	118.6 (3)	C5–N13–N14	109.0 (2)
N13–C5–N17	134.5 (3)	C5–N13–H13	125.5
C2–N1–N2	108.4 (3)	N14–N13–H13	125.5
C1–N2–N1	107.4 (3)	N15–N14–N13	106.2 (3)
C1–N3–C2	104.7 (3)	N14–N15–N16	111.2 (3)
C1–N3–N5	121.7 (3)	C5–N16–N15	106.7 (3)
C2–N3–N5	133.6 (2)	N18–N17–C5	117.2 (3)
C1–N4–H4A	122 (3)	O2–N18–O1	121.6 (3)
C1–N4–H4B	120 (3)	O2–N18–N17	117.6 (3)
H4A–N4–H4B	118 (4)	O1–N18–N17	120.8 (3)
N3–N5–H5A	107 (3)	H3O1–O3–H3O2	113 (3)
N3–N5–H5B	107 (3)	H4O1–O4–H4O2	106 (3)
H5A–N5–H5B	106 (4)	H5O1–O5–H5O2	109 (3)
N7–N6–C2	114.7 (3)	H6O1–O6–H6O2	114 (3)
N6–N7–C3	111.9 (3)		
N6–C2–N1–N2	-179.8 (3)	N10–C4–N9–N8	0.4 (3)
N3–C2–N1–N2	-0.1 (3)	C3–N8–N9–C4	0.2 (3)

N4–C1–N2–N1	178.9 (3)	N11–C4–N10–C3	179.5 (3)
N3–C1–N2–N1	0.4 (3)	N9–C4–N10–C3	-0.9 (3)
C2–N1–N2–C1	-0.2 (3)	N11–C4–N10–N12	3.0 (5)
N4–C1–N3–C2	-179.0 (3)	N9–C4–N10–N12	-177.4 (3)
N2–C1–N3–C2	-0.5 (3)	N8–C3–N10–C4	1.1 (4)
N4–C1–N3–N5	2.0 (5)	N7–C3–N10–C4	-178.2 (3)
N2–C1–N3–N5	-179.5 (3)	N8–C3–N10–N12	177.3 (3)
N1–C2–N3–C1	0.4 (3)	N7–C3–N10–N12	-2.0 (5)
N6–C2–N3–C1	-180.0 (3)	N16–C5–N13–N14	0.1 (3)
N1–C2–N3–N5	179.2 (3)	N17–C5–N13–N14	178.9 (4)
N6–C2–N3–N5	-1.2 (6)	C5–N13–N14–N15	-0.1 (3)
N1–C2–N6–N7	179.2 (3)	N13–N14–N15–N16	0.1 (4)
N3–C2–N6–N7	-0.4 (5)	N13–C5–N16–N15	0.0 (3)
C2–N6–N7–C3	-179.1 (3)	N17–C5–N16–N15	-179.1 (3)
N8–C3–N7–N6	3.1 (5)	N14–N15–N16–C5	0.0 (4)
N10–C3–N7–N6	-177.8 (3)	N16–C5–N17–N18	179.4 (3)
N10–C3–N8–N9	-0.8 (3)	N13–C5–N17–N18	0.7 (6)
N7–C3–N8–N9	178.4 (3)	C5–N17–N18–O2	178.9 (3)
N11–C4–N9–N8	-180.0 (3)	C5–N17–N18–O1	-1.1 (5)

Single Crystal XRD data for 4,4',5,5' tetra-amino-3,3'-azo bis-1,2,4-triazolium 5 nitrimino-1,2,3,4-tetrazolate methanolate (TAABTH CHN_6O_2•MeOH)[(6•MeOH •0.5($C_4H_8N_{12}$)]



View of the structure of **6•MeOH •0.5$C_4H_8N_{12}$**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Symmetry code: (*a*) 1 − *x*, 1 − *y*, 1 − *z*.

Crystal data

$C_4H_8N_{12}·0.5(C_4H_{10}N_{12})·CHN_6O_2·CH_4O$	$Z = 2$
$M_r = 498.46$	$F(000) = 516$
Triclinic, $P\bar{1}$	$D_x = 1.669$ Mg m^{-3}
$a = 8.3500$ (11) Å	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$b = 10.7574$ (17) Å	Cell parameters from 2437 reflections

c = 12.0071 (16) Å	θ = 4.0–69.9°
α = 104.533 (10)°	μ = 1.17 mm^{-1}
β = 107.050 (9)°	T = 150 K
γ = 91.66 (1)°	Needle, yellow
V = 992.0 (3) Å^3	0.20 × 0.03 × 0.01 mm

Data collection

Bruker AXS D8 Quest diffractometer with PhotonII CPAD detector	9304 measured reflections
Radiation source: I-mu-S microsource X-ray tube	3831 independent reflections
Laterally graded multilayer (Goebel) mirror monochromator	2108 reflections with $I > 2\sigma(I)$
Detector resolution: 7.4074 pixels mm^{-1}	R_{int} = 0.117
ω and phi scans	θ_{max} = 80.1°, θ_{min} = 4.0°
Absorption correction: multi-scan, *SADABS 2016/2, Krause et al., 2015*	h = -9→10
T_{min} = 0.613, T_{max} = 0.754	k = -12→13
	l = -15→15

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.061	Hydrogen site location: mixed
$wR(F^2)$ = 0.165	H atoms treated by a mixture of indep. and constr. refinement
S = 0.90	$w = 1/[\sigma^2(F_o^2)]$ where $P = (F_o^2 + 2F_c^2)/3$
3831 reflections	$(\Delta/\sigma)_{max} < 0.001$
359 parameters	$\Delta\rho_{max}$ = 0.46 e Å^{-3}
12 restraints	$\Delta\rho_{min}$ = -0.41 e Å^{-3}

Geometric parameters (Å, º) for 6•MeOH •0.5C$_4$H$_8$N$_{12}$

C1–N4	1.333 (5)	N1A–N2A	1.370 (4)
C1–N1	1.353 (4)	N3A–N5A	1.414 (4)
C1–N5	1.364 (4)	N4A–H4A	0.874 (19)
C2–O3	1.428 (4)	N4A–H4B	0.896 (19)
C2–H2C	0.9800	N5A–H5A	0.907 (19)
C2–H2D	0.9800	N5A–H5B	0.888 (19)
C2–H2E	0.9800	N6A–N7A	1.277 (3)
N1–N2	1.337 (4)	N8A–N9A	1.360 (4)

N1–H1	0.8800	N10A–N12A	1.413 (4)
N2–N3	1.306 (4)	N11A–H11A	0.877 (19)
N3–N4	1.355 (4)	N11A–H11B	0.889 (19)
N5–N6	1.314 (4)	N12A–H12A	0.888 (19)
N6–O2	1.253 (3)	N12A–H12B	0.895 (19)
N6–O1	1.262 (4)	C1B–N4B	1.329 (4)
O3–H3	0.8400	C1B–N2B	1.334 (4)
C1A–N4A	1.319 (5)	C1B–N3B	1.347 (4)
C1A–N2A	1.344 (4)	C2B–N1B	1.300 (4)
C1A–N3A	1.358 (4)	C2B–N6B	1.381 (4)
C2A–N1A	1.315 (4)	C2B–N3B	1.389 (4)
C2A–N6A	1.370 (5)	N1B–N2B	1.370 (4)
C2A–N3A	1.383 (4)	N2B–H2B	0.8800
C3A–N8A	1.313 (4)	N3B–N5B	1.405 (3)
C3A–N7A	1.379 (5)	N4B–H4C	0.875 (19)
C3A–N10A	1.384 (4)	N4B–H4D	0.877 (19)
C4A–N11A	1.314 (5)	N5B–H5C	0.892 (19)
C4A–N9A	1.345 (4)	N5B–H5D	0.891 (19)
C4A–N10A	1.349 (4)	N6B–N6B^{i}	1.269 (5)
N4–C1–N1	108.0 (3)	C1A–N4A–H4B	123 (3)
N4–C1–N5	119.8 (3)	H4A–N4A–H4B	120 (4)
N1–C1–N5	132.2 (4)	N3A–N5A–H5A	98 (2)
O3–C2–H2C	109.5	N3A–N5A–H5B	113 (3)
O3–C2–H2D	109.5	H5A–N5A–H5B	110 (4)
H2C–C2–H2D	109.5	N7A–N6A–C2A	114.2 (3)
O3–C2–H2E	109.5	N6A–N7A–C3A	113.7 (3)
H2C–C2–H2E	109.5	C3A–N8A–N9A	107.1 (3)
H2D–C2–H2E	109.5	C4A–N9A–N8A	109.0 (3)
N2–N1–C1	108.8 (3)	C4A–N10A–C3A	106.1 (3)
N2–N1–H1	125.6	C4A–N10A–N12A	122.0 (3)
C1–N1–H1	125.6	C3A–N10A–N12A	131.9 (3)
N3–N2–N1	106.4 (3)	C4A–N11A–H11A	111 (3)
N2–N3–N4	111.2 (3)	C4A–N11A–H11B	117 (3)
C1–N4–N3	105.6 (3)	H11A–N11A–H11B	130 (4)
N6–N5–C1	116.6 (3)	N10A–N12A–H12A	107 (3)

O2–N6–O1	119.6 (3)	N10A–N12A–H12B	106 (3)
O2–N6–N5	118.1 (3)	H12A–N12A–H12B	109 (4)
O1–N6–N5	122.3 (3)	N4B–C1B–N2B	127.4 (3)
C2–O3–H3	109.5	N4B–C1B–N3B	124.8 (3)
N4A–C1A–N2A	127.1 (3)	N2B–C1B–N3B	107.8 (3)
N4A–C1A–N3A	123.1 (3)	N1B–C2B–N6B	119.4 (3)
N2A–C1A–N3A	109.8 (3)	N1B–C2B–N3B	110.6 (3)
N1A–C2A–N6A	120.6 (3)	N6B–C2B–N3B	130.0 (3)
N1A–C2A–N3A	109.4 (3)	C2B–N1B–N2B	106.0 (3)
N6A–C2A–N3A	129.9 (3)	C1B–N2B–N1B	109.9 (3)
N8A–C3A–N7A	119.8 (3)	C1B–N2B–H2B	125.1
N8A–C3A–N10A	109.7 (3)	N1B–N2B–H2B	125.1
N7A–C3A–N10A	130.4 (3)	C1B–N3B–C2B	105.7 (3)
N11A–C4A–N9A	126.5 (3)	C1B–N3B–N5B	121.4 (3)
N11A–C4A–N10A	125.5 (3)	C2B–N3B–N5B	132.8 (3)
N9A–C4A–N10A	108.0 (3)	C1B–N4B–H4C	119 (3)
C2A–N1A–N2A	108.6 (3)	C1B–N4B–H4D	111 (3)
C1A–N2A–N1A	106.8 (3)	H4C–N4B–H4D	127 (4)
C1A–N3A–C2A	105.3 (3)	N3B–N5B–H5C	105 (3)
C1A–N3A–N5A	121.0 (3)	N3B–N5B–H5D	105 (3)
C2A–N3A–N5A	133.7 (3)	H5C–N5B–H5D	109 (4)
C1A–N4A–H4A	115 (3)	N6B^{i}–N6B–C2B	113.8 (4)
N4–C1–N1–N2	-1.5 (4)	N7A–C3A–N8A–N9A	177.8 (3)
N5–C1–N1–N2	176.2 (4)	N10A–C3A–N8A–N9A	0.2 (4)
C1–N1–N2–N3	1.1 (4)	N11A–C4A–N9A–N8A	179.6 (3)
N1–N2–N3–N4	-0.4 (4)	N10A–C4A–N9A–N8A	-1.1 (4)
N1–C1–N4–N3	1.2 (4)	C3A–N8A–N9A–C4A	0.6 (4)
N5–C1–N4–N3	-176.8 (3)	N11A–C4A–N10A–C3A	-179.5 (3)
N2–N3–N4–C1	-0.5 (4)	N9A–C4A–N10A–C3A	1.2 (4)
N4–C1–N5–N6	-178.8 (3)	N11A–C4A–N10A–N12A	-1.2 (6)
N1–C1–N5–N6	3.8 (6)	N9A–C4A–N10A–N12A	179.5 (3)
C1–N5–N6–O2	-176.7 (3)	N8A–C3A–N10A–C4A	-0.9 (4)
C1–N5–N6–O1	4.8 (5)	N7A–C3A–N10A–C4A	-178.2 (4)
N6A–C2A–N1A–N2A	179.5 (3)	N8A–C3A–N10A–N12A	-178.9 (3)
N3A–C2A–N1A–N2A	0.0 (4)	N7A–C3A–N10A–N12A	3.8 (6)

N4A–C1A–N2A–N1A	178.1 (4)	N6B–C2B–N1B–N2B	-179.3 (3)
N3A–C1A–N2A–N1A	0.5 (4)	N3B–C2B–N1B–N2B	1.0 (4)
C2A–N1A–N2A–C1A	-0.3 (4)	N4B–C1B–N2B–N1B	178.0 (4)
N4A–C1A–N3A–C2A	-178.2 (3)	N3B–C1B–N2B–N1B	-0.4 (4)
N2A–C1A–N3A–C2A	-0.5 (4)	C2B–N1B–N2B–C1B	-0.4 (4)
N4A–C1A–N3A–N5A	-0.2 (5)	N4B–C1B–N3B–C2B	-177.4 (3)
N2A–C1A–N3A–N5A	177.5 (3)	N2B–C1B–N3B–C2B	1.0 (4)
N1A–C2A–N3A–C1A	0.3 (4)	N4B–C1B–N3B–N5B	1.5 (5)
N6A–C2A–N3A–C1A	-179.1 (4)	N2B–C1B–N3B–N5B	179.8 (3)
N1A–C2A–N3A–N5A	-177.3 (3)	N1B–C2B–N3B–C1B	-1.3 (4)
N6A–C2A–N3A–N5A	3.2 (6)	N6B–C2B–N3B–C1B	179.1 (4)
N1A–C2A–N6A–N7A	178.8 (3)	N1B–C2B–N3B–N5B	-180.0 (3)
N3A–C2A–N6A–N7A	-1.8 (5)	N6B–C2B–N3B–N5B	0.4 (6)
C2A–N6A–N7A–C3A	179.3 (3)	N1B–C2B–N6B–N6B^{i}	-178.2 (4)
N8A–C3A–N7A–N6A	-172.0 (3)	N3B–C2B–N6B–N6B^{i}	1.4 (6)
N10A–C3A–N7A–N6A	5.1 (5)		

Symmetry code: (i) -*x*+1, -*y*+1, -*z*+1.

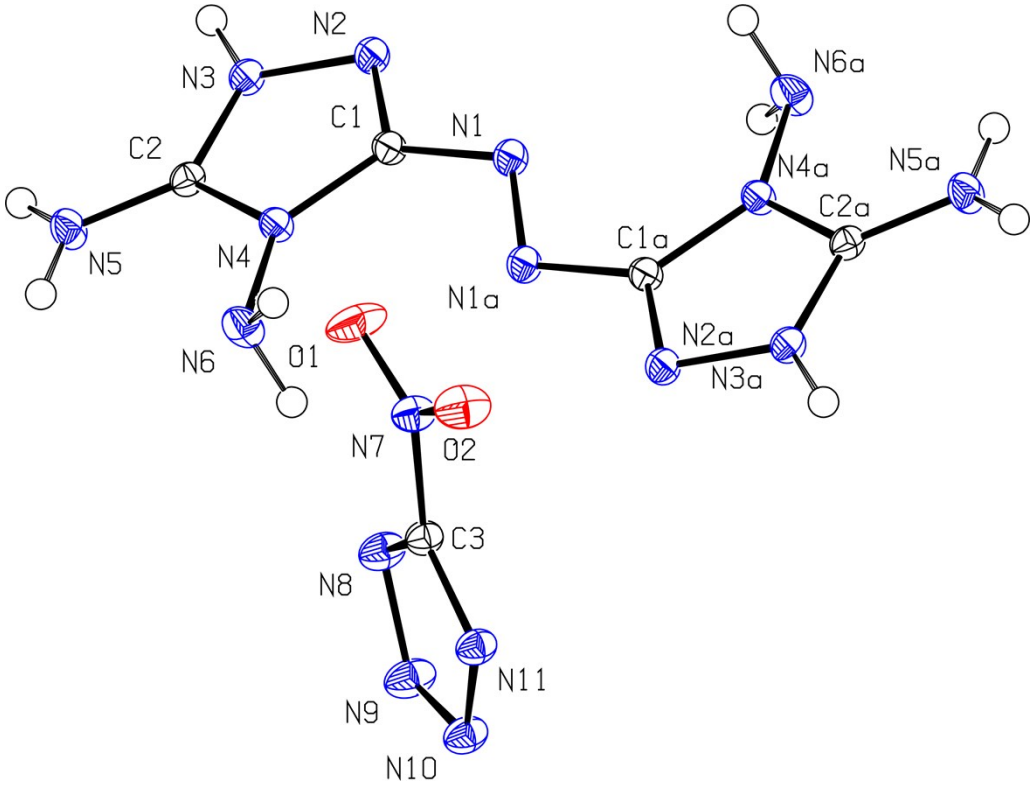
Hydrogen-bond geometry (Å, º) for 6•MeOH •0.5C$_4$H$_8$N$_{12}$

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
C2–H2*E*···N1^{ii}	0.98	2.67	3.460 (5)	138
N1–H1···O1	0.88	2.07	2.548 (4)	113
N1–H1···N1*A*^{iii}	0.88	2.12	2.945 (4)	157
O3–H3···N5	0.84	1.97	2.781 (4)	161
N4*A*–H4*A*···O2^{iv}	0.87 (2)	2.63 (3)	3.328 (4)	138 (4)
N4*A*–H4*B*···N2*A*^{v}	0.90 (2)	2.12 (2)	2.984 (4)	162 (4)
N5*A*–H5*A*···N1*B*	0.91 (2)	2.20 (2)	3.049 (4)	156 (3)
N5*A*–H5*B*···N1*A*^{vi}	0.89 (2)	2.69 (3)	3.416 (4)	140 (3)
N11*A*–H11*A*···N12*A*^{vii}	0.88 (2)	2.34 (4)	2.990 (5)	131 (4)
N11*A*–H11*B*···N2^{viii}	0.89 (2)	2.66 (4)	3.301 (5)	130 (3)
N11*A*–H11*B*···N3^{viii}	0.89 (2)	2.07 (2)	2.911 (4)	158 (4)
N12*A*–H12*A*···O1^{vii}	0.89 (2)	2.40 (4)	3.017 (5)	127 (3)
N12*A*–H12*A*···N4*A*^{vi}	0.89 (2)	2.60 (3)	3.346 (5)	142 (3)
N12*A*–H12*B*···N2^{iii}	0.90 (2)	2.50 (3)	3.110 (4)	126 (3)
N12*A*–H12*B*···N6*A*	0.90 (2)	2.38 (4)	2.907 (5)	118 (3)

N2*B*–H2*B*···N9*A*^{ix}	0.88	1.81	2.653 (4)	160
N4*B*–H4*C*···O3^{ix}	0.88 (2)	2.00 (2)	2.867 (4)	170 (4)
N4*B*–H4*D*···O2^{ii}	0.88 (2)	2.21 (3)	3.012 (4)	151 (4)
N4*B*–H4*D*···N5*B*	0.88 (2)	2.43 (4)	2.841 (4)	109 (3)
N5*B*–H5*C*···N8*A*^{i}	0.89 (2)	2.39 (3)	3.113 (5)	139 (3)
N5*B*–H5*D*···O3	0.89 (2)	2.29 (2)	3.152 (4)	163 (4)

Symmetry codes: (i) -*x*+1, -*y*+1, -*z*+1; (ii) -*x*+1, -*y*+2, -*z*+1; (iii) -*x*+1, -*y*+2, -*z*+2; (iv) *x*-1, *y*-1, *z*; (v) -*x*, -*y*+1, -*z*+2; (vi) -*x*+1, -*y*+1, -*z*+2; (vii) -*x*+2, -*y*+2, -*z*+2; (viii) *x*+1, *y*, *z*; (ix) *x*-1, *y*, *z*.

Single Crystal XRD data for 4,4',5,5' tetra-amino-3,3'-azo bis-1,2,4-triazolium di-5-nitro-1,2,3,4-tetrazolate [HTAABTH $(CN_5O_2)_2$] (7)



View of the structure of **7**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Symmetry code: (*a*) − *x*, 1 − *y*, 1 − *z*.

Crystal data

$C_4H_{10}N_{12}·2(CN_5O_2)$	$F(000)$ = 464
M_r = 454.36	D_x = 1.762 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 5.5317 (3) Å	Cell parameters from 9945 reflections
b = 14.9646 (8) Å	θ = 2.4–33.0°
c = 10.6648 (5) Å	μ = 0.15 mm^{-1}
β = 104.0683 (18)°	T = 150 K
V = 856.35 (8) Å^3	Needle, orange
Z = 2	0.55 × 0.23 × 0.19 mm

Data collection

Bruker AXS D8 Quest CMOS diffractometer	28936 measured reflections

Radiation source: fine focus sealed tube X-ray source	3287 independent reflections
Triumph curved graphite crystal monochromator	2692 reflections with $I > 2\sigma(I)$
Detector resolution: 10.4167 pixels mm^{-1}	$R_{int} = 0.036$
ω and phi scans	$\theta_{max} = 33.2°$, $\theta_{min} = 2.7°$
Absorption correction: multi-scan, *SADABS* 2016/2, Krause et al., 2015	$h = -7 \rightarrow 8$
$T_{min} = 0.718$, $T_{max} = 0.747$	$k = -23 \rightarrow 23$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.037$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.101$	All H-atom parameters refined
$S = 1.05$	$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 0.3171P]$ where $P = (F_o^2 + 2F_c^2)/3$
3287 reflections	$(\Delta/\sigma)_{max} = 0.001$
166 parameters	$\Delta\rho_{max} = 0.47$ e $Å^{-3}$
0 restraints	$\Delta\rho_{min} = -0.27$ e $Å^{-3}$
Extinction coefficient: 0.007 (2)	Extinction correction: *SHELXL2018*/3 (Sheldrick, 2018), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Geometric parameters (Å, º) for 7

C1–N2	1.3086 (11)	N3–H3	0.897 (16)
C1–N4	1.3849 (11)	N4–N6	1.4033 (11)
C1–N1	1.3860 (11)	N5–H5A	0.880 (18)
C2–N5	1.3141 (12)	N5–H5B	0.869 (17)
C2–N3	1.3425 (12)	N6–H6A	0.920 (17)
C2–N4	1.3561 (11)	N6–H6B	0.933 (19)
C3–N8	1.3238 (12)	N7–O1	1.2243 (11)
C3–N11	1.3266 (11)	N7–O2	1.2268 (11)
C3–N7	1.4397 (12)	N8–N9	1.3429 (12)
N1–N1^{i}	1.2723 (15)	N9–N10	1.3265 (12)
N2–N3	1.3663 (11)	N10–N11	1.3419 (11)
N2–C1–N4	111.18 (7)	C2–N4–N6	121.00 (8)
N2–C1–N1	119.25 (8)	C1–N4–N6	132.46 (7)
N4–C1–N1	129.56 (8)	C2–N5–H5A	119.3 (11)

N5–C2–N3	129.19 (8)	C2–N5–H5B	120.4 (11)
N5–C2–N4	124.98 (8)	H5A–N5–H5B	120.1 (16)
N3–C2–N4	105.83 (8)	N4–N6–H6A	107.7 (10)
N8–C3–N11	114.51 (8)	N4–N6–H6B	108.2 (11)
N8–C3–N7	121.62 (8)	H6A–N6–H6B	105.8 (15)
N11–C3–N7	123.87 (8)	O1–N7–O2	124.83 (9)
N1^{i}–N1–C1	113.49 (9)	O1–N7–C3	117.47 (8)
C1–N2–N3	104.55 (7)	O2–N7–C3	117.70 (8)
C2–N3–N2	111.90 (7)	C3–N8–N9	103.37 (8)
C2–N3–H3	128.2 (11)	N10–N9–N8	109.20 (8)
N2–N3–H3	119.6 (11)	N9–N10–N11	110.09 (8)
C2–N4–C1	106.48 (7)	C3–N11–N10	102.82 (7)
N2–C1–N1–N1^{i}	-167.60 (10)	N2–C1–N4–N6	-174.78 (9)
N4–C1–N1–N1^{i}	11.43 (16)	N1–C1–N4–N6	6.13 (17)
N4–C1–N2–N3	-2.19 (10)	N8–C3–N7–O1	4.50 (14)
N1–C1–N2–N3	177.01 (8)	N11–C3–N7–O1	-175.63 (10)
N5–C2–N3–N2	-179.55 (9)	N8–C3–N7–O2	-175.41 (9)
N4–C2–N3–N2	0.47 (10)	N11–C3–N7–O2	4.46 (14)
C1–N2–N3–C2	1.07 (10)	N11–C3–N8–N9	-0.24 (11)
N5–C2–N4–C1	178.28 (9)	N7–C3–N8–N9	179.65 (9)
N3–C2–N4–C1	-1.74 (10)	C3–N8–N9–N10	0.32 (11)
N5–C2–N4–N6	-4.02 (14)	N8–N9–N10–N11	-0.30 (12)
N3–C2–N4–N6	175.96 (8)	N8–C3–N11–N10	0.06 (11)
N2–C1–N4–C2	2.55 (10)	N7–C3–N11–N10	-179.82 (9)
N1–C1–N4–C2	-176.54 (9)	N9–N10–N11–C3	0.15 (11)

Symmetry code: (i) -*x*, -*y*+1, -*z*+1.

Hydrogen-bond geometry (Å, º) for 7

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
N3–H3···N8^{ii}	0.897 (16)	1.928 (17)	2.8207 (11)	173.3 (15)
N5–H5*A*···N10^{iii}	0.880 (18)	2.099 (18)	2.9493 (12)	162.1 (15)
N5–H5*B*···N9^{iv}	0.869 (17)	2.158 (17)	2.9130 (12)	145.1 (15)
N6–H6*A*···N11^{v}	0.920 (17)	2.333 (17)	3.2429 (12)	170.0 (14)
N6–H6*B*···O2^{v}	0.933 (19)	2.415 (17)	2.8922 (11)	111.7 (13)

Symmetry codes: (ii) -*x*+1, -*y*+1, -*z*+2; (iii) -*x*+2, *y*+1/2, -*z*+3/2; (iv) -*x*+2, -*y*+1, -*z*+2; (v) -*x*+1, -*y*+1, -*z*+1.

References

1. R. G. Child. *J. Heterocycl. Chem*. 1965, **2**, 98.
2. T. M. Klapötke, J. Stierstorfer. *Helv. Chimica Acta.* 2007, 90(11), 2132.
3. T. M. Klapötke, D. G. Piercey, N. Meheta, K. D. Oyler, M. Jorgensen, S. Lenahan, J. S. Salan, J. W. Fronabarger, M. D. Williams. *Zeit. Anorg. Allg. Chem.* 2013, **639** (5), 681-688.
4. Description - ElectraSyn 2.0 Package. Can be found under: https://www.ika.com/en/Products-Lab-Eq/Electrochemistry-Kit-csp-516/ElectraSyn-20-Package-cpdt-20008980/
5. J. L. Dempsey. *J. Chem. Educ.* 2017, **95** (2), 197.
6. Bruker. Apex3 v2018.7-2, Saint V8.38A, Bruker AXS Inc.: Madison (WI), USA 2018.
7. L. Krause., R. Herbst-Irmer, G. M. Sheldrick, D. Stalke. *J. Appl. Cryst.* 2015, **48**, 3-10.
8. G. M. Sheldrick. *Acta Crystallogr A.* 2008, **64**(1), 112–122.
9. G. M. Sheldrick. *Acta Crystallogr Sect C Struct. Chem.* 2015**, 71**(1), 3–8.