Short communication

Studies on energetic compounds
Part 45. Synthesis and crystal structure of disodium azotetrazole pentahydrate

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Abstract

A disodium salt of azotetrazolate (SAZ) has been prepared and characterized by elemental, UV, ^{13}C NMR, FT-IR, and crystallographic analyses. Single crystals of the pentahydrate were grown by slow evaporation of an aqueous solution under reduced pressure. The crystal structure of SAZ has been determined by X-ray diffraction. The crystal lattice is triclinic P$\bar{1}$ (no. 2) with lattice parameters $a = 7.115(1)$ Å, $b = 7.559(1)$ Å, $c = 12.025(1)$ Å, $\alpha = 79.75(1)°$, $\beta = 81.12(1)°$, $\gamma = 68.16(1)°$ and $V = 587.97(12)$ Å^3. Explosion delay studies have been undertaken using the tube furnace technique. The thermal stability of the compound has been discussed in the light of TG-DSC and explosion delay.
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Keywords: SAZ; Single crystal; XRD; Crystal structure; Explosion delay

1. Introduction

Research in the field of high energetic materials frequently emphasises the preparation of organic energetic materials containing the nitro-groups. The nitro-groups are capable of oxidizing the carbon and hydrogen atoms in the molecule to water and to oxides of carbon, all of which have very negative heats of formation. In spite of this, there are very few examples, even for highly nitrated molecules, which possess enough oxygen to completely oxidise the carbon in the backbone to carbon dioxide. As a consequence, these materials typically produce significant quantities of residue and smoke from the solid carbon and unoxidised organics produced during detonation or combustion.

On the other hand, highly energetic compounds rich in nitrogen content represent a new and unexplored class of compounds. They rely on their highly efficient gas production and also on their high heat of formation for energy release, since elemental nitrogen, which has a zero heat of formation, is the major product of decomposition. In comparison to common high explosives, high nitrogen content compounds produce more gas per gram [1]. These compounds are prospective materials for the generation of gases as blowing agents, solid propellant and other combustible and thermally decomposing system [2,3]. In a continuation of our research programme on high energetic materials, the present paper deals with the synthesis and the crystal structure characterization of the high nitrogen content salt, disodium azotetrazole pentahydrate.

2. Experimental

2.1. Materials

5-Aminotetrazole monohydrate (Biochemistry grade, Spectrochem), KMnO$_4$ (s.d.fine), NaOH pellets (s.d.fine) are commercially available and were used as received.

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Table 1
Physio-chemical properties of SAZ

Techniques	Result
Elemental analysis (% observed, calculated values in parenthesis)	
C	7.96 (7.79)
H	3.39 (3.38)
N	46.61 (46.63)
Na	18.32 (18.65)
UV (nm)	197, 315, 324, 333, 470
FT-IR (cm^{-1})	3430 (O—H), 1452 (C=N), 1401 (C—N), 1203, 1165, 1065, 774 (azotetrazolate), 528 (Na—N), 740 (Na—O)
^{13}C NMR	173
DSC (°C)	
Endothermic peak	78.0, 122.7
Exothermic peak	276.8

2.2. Synthesis

The oxidation of 5-aminotetrazole monohydrate with potassium permanganate in sodium hydroxide solution at 60–70 °C gives yellow crystals of the target compound with an overall yield of 75–78%.

2.3. Elemental, spectroscopic and thermal analyses

The C, H, N, analyses were done with Heraeus Carlo Erba 1108 instrument. The UV spectra were recorded with Analytic-Jena SPECORD 200 (Germany) spectrophotometer in 200–700 nm range. FT-IR spectra were taken with Perkin Elmer RXI Spectrometer using KBr pellets in the range of 400–4000 cm^{-1}. The ^{13}C NMR spectra were recorded using a DMSO-d$_6$ Em 390 (Varian), while TG-DSC measurement were carried out simultaneously with a STA 409 PC (NETZSCH, Germany) instrument in N$_2$ atmosphere. The elemental, UV, FT-IR, ^{13}C NMR and DSC data are given in Table 1.

2.4. X-ray data collection and structure determination

Crystals of SAZ suitable for X-ray diffraction were obtained directly by recrystallization from aqueous solution. The measurements of crystal data were performed at low temperature (−75 °C) using a Nonius Kappa CCD diffractometer, equipped with a rotating anode generator, the Nonius FR 591. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN [4]. The structure was solved by direct methods (Program SHELXS-97 [5]) and refined by full-matrix least squares method on all F^2 data using SHELXL-97 [6]. Hydrogen atoms were located from a difference Fourier map and refined independently. Several cycles of refinement of the coordinates with anisotropic thermal parameters for non-hydrogen atoms and isotropic parameters for H atoms reduced the R-value to 0.045.

2.5. Explosion delay (D$_E$) studies

Explosion delay of the compound are recorded using tube furnace (TF) technique [7]. The details of the experiment are as reported earlier [7,8]. The D$_E$ data were found to be fit in the following equation [9,10]

$$D_E = A\,e^{E^*/RT}$$

where E^* is the activation energy and T the absolute temperature. The explosion delay data are summarized in Table 2. The value of E^* was obtained from the slope of the plot of $\ln D_E$ versus $1/T$.

3. Result and discussion

Elemental analysis data obtained from SAZ matches with the theoretically calculated values with an accuracy of ±1%. The UV spectrum showed absorption bands in the ultraviolet and visible region due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions (Table 1). The FT-IR spectrum of SAZ showed an asymmetric C—N ring stretching vibration at 1401 cm^{-1} and an asymmetric C—N stretching mode of the azo group at 734 cm^{-1}; in addition to peaks attributable to hydroxyl group at 3430 cm^{-1} corresponding to stretching frequency (comparatively at lower frequency as oxygen is coordinated with sodium atom) while the sharp peak at 528 cm^{-1} is indicative of Na—N bonding and the peak at 740 cm^{-1} is due to Na—O stretching.

A projection of the dimeric structural arrangement of SAZ is given in Fig. 1. Pertinent crystallographic data and the experimental parameters are presented in Table 3, while the bond lengths are listed in Table 4.

The compound crystallizes in the triclinic space group P$\bar{1}$ (no. 2) with lattice parameters $a = 7.115(1)$ Å, $b = 7.559(1)$ Å, $c = 12.025(1)$ Å, $\alpha = 79.75(1)°$, $\beta = 81.12(1)°$, $\gamma = 68.16(1)°$, $V = 587.97(12)$ Å^3, $Z = 2$, $D_X = 1.696$ g cm^{-3}.

The structure is built up from isolated azotetrazolate dianions and sodium cations. The adjacent molecules form a chain wherein the crystal waters act as a bridging molecules between the cations (a dimer from this chain is shown in Fig. 1). The tetrazole rings are almost planar. N—N bond lengths in the tetrazole rings are quite similar and vary from 1.311(2) to 1.337(2).
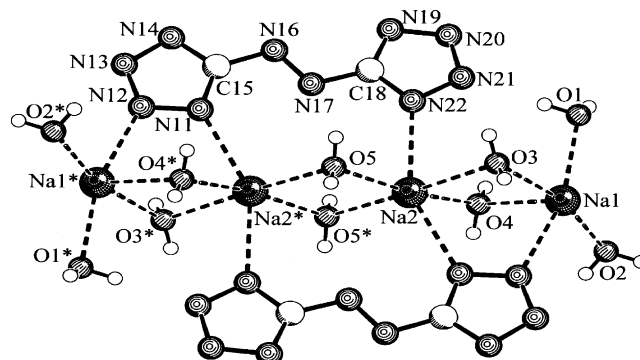

Fig. 1. Crystal structure of disodium azotetrazole pentahydrate.

Table 2
Explosion delay (D_E) and activation energy for thermal explosion (E^*) for SAZ

D_E (s) at various temperatures (°C)						E^* (kJ mol^{-1})	$\ln A$	r
325 ± 1	350 ± 1	375 ± 1	400 ± 1	425 ± 1	450 ± 1			
135	95	84	70	56	52	27.1	-0.59	0.9897

One of the most interesting aspects of this structure is the formation of infinite chains in the $[-1\,0\,1]$ direction. Both sodium atoms are hexacoordinated, and help to bridge the dimers in the chain, along with the shared water molecules. Along the chains, there are Na···Na distances of Na1···Na1*, 3.383(2) Å, Na1···Na2, 3.517(1) Å and Na2···Na2*, 3.618(1) Å. Adjacent chains are connected by very weak Na···N connections greater than 3.5 Å.

To understand the thermal stability of energetic compounds, the measurement of explosion delay and evaluating the kinetic parameters (Table 2) there from is an effective method [11]. Computational calculation shows that the activation energy for explosion is 27.1 kJ mol^{-1}.

The results of TG show that the compound undergo an approximately 100% weight loss in nitrogen atmosphere and only a very small amount ($\approx$1.9%) of residue remained after heating to 454 °C. The compound decomposes in three steps, Firstly, there are two weight losses due to removal of waters which are then immediately followed by a third step of decomposition taking place gradually from 240 to 300 °C which might be due to ring rupture. Simultaneous DSC measurements of SAZ at 10 °C min^{-1} (in N$_2$ atmosphere, flow rate 60 mL/min) show a sharp endotherm at 122.7 °C indicating the melting of the compound followed by an exotherm

Table 4
Bond lengths (Å) for SAZ

Na(1)—O(2)	2.376(2)
Na(1)—O(1)	2.380(2)
Na(1)—O(4)	2.393(2)
Na(1)—N(12) #2	2.460(2)
Na(1)—O(3)	2.458(2)
Na(1)—Na(1) #1	3.383(2)
Na(1)—Na(2)	3.517(1)
Na(2)—O(4)	2.413(2)
Na(2)—O(5)	2.426(2)
Na(2)—O(5) #2	2.466(2)
Na(2)—O(3)	2.483(2)
Na(2)—N(11) #2	2.519(2)
Na(2)—N(22)	2.560(2)
Na(2)—Na(2) #2	3.618(1)
N(11)—C(15)	1.327(2)
N(11)—N(12)	1.334(2)
N(12)—N(13)	1.311(2)
N(13)—N(14)	1.337(2)
N(14)—C(15)	1.331(2)
C(15)—N(16)	1.403(2)
N(16)—N(17)	1.257(2)
N(17)—C(18)	1.398(2)
C(18)—N(19)	1.329(2)
C(18)—N(22)	1.333(2)
N(19)—N(20)	1.335(2)
N(20)—N(21)	1.322(2)
N(21)—N(22)	1.328(2)

Symmetry transformations used to generate equivalent atoms. #1: $-x+2$, $-y+1$, $-z-1$, #2: $-x+1$, $-y+1/2$, $-z$.

at 276.8 °C, which may be attributed to the exothermal decomposition of SAZ. However an additional weak endotherm peak at 78 °C is not easily explained; it may be due to moisture.

Table 3
Crystal data and summary of intensity and structure refinement data for SAZ

Empirical formula	C$_2$H$_{10}$N$_{10}$Na$_2$O$_5$
CCDC deposit no.	235627
Colour	Yellow
Formula weight	300.18
T (K)	198
λ (Å)	0.71073
Crystal system	Triclinic
Space group	P$\bar{1}$ (no. 2)
Crystal size	$0.55 \times 0.40 \times 0.15$
Cell constants	$a = 7.115(1)$ Å, $\alpha = 79.75(1)°$
	$b = 7.559(1)$ Å, $\beta = 81.12(1)°$
	$c = 12.025(1)$ Å, $\gamma = 68.16(1)°$
Z, calculated density (g cm^{-3})	2, 1.696
μ (cm^{-1})	2.11
F (000)	308
Monochromater	Graphite
θ range for data collection	$1.73–28.86°$
Limiting indices	$-9 \leq h \leq 9$, $-8 \leq k \leq 10$, $-15 \leq l < 16$
Reflections collected/unique	6254/2794 [$R_{(int)} = 0.051$]
Data/restraints/parameters	2794/0/212
Goodness-of-fit on F^2	1.0531
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0447$, $wR_2 = 0.1040$
R indices (all data)	$R_1 = 0.0531$, $wR_2 = 0.1092$
Largest diff. peak and hole (e Å^{-3})	0.323, -0.283

Appendix A. Supplementary material

CCDC 235627 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdc.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB21EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk.

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