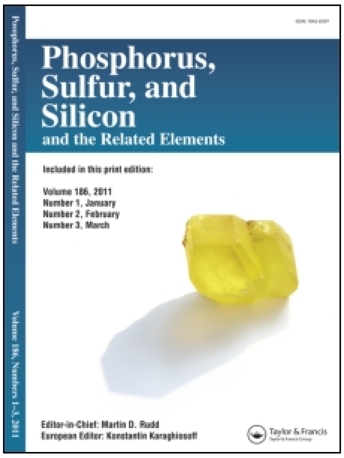

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The Synthesis and Some Properties of Diammonium Hydrogentrisulfimide (Diammonium 2-Hydrogen,1,3,5,2,4,6-Trithiatriazine,1,1,3,3,5,5-Hexoxide), (NH 4) 2 HN 3 S 3 O 6 , and the X-Ray Structure of the Hydrogentrisulfimide Ion

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THE SYNTHESIS AND SOME PROPERTIES OF DIAMMONIUM HYDROGENTRISULFIMIDE (DIAMMONIUM 2-HYDROGEN,1,3,5,2,4,6-TRITHIATRIAZINE,1,1,3,3,5,5-HEXOXIDE), $(NH_4)_2HN_3S_3O_6$, AND THE X-RAY STRUCTURE OF THE HYDROGENTRISULFIMIDE ION

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The reaction of stoichiometric amounts of $(NH_4)_3N_3S_3O_6$ *and* HNO_3 *produces* $(NH_4)_2HN_3S_3O_6$*. Its low acidity decreases the amount of acid-catalyzed hydrolysis and allows the isolation of its crystals. The distorting effects of monoprotonation such as S—N, 1.594(7) Å, and* $S—N_H$*, 1.690(9) Å, in the* $HN_3S_3O_6^{2-}$ *ring are described and discussed.*

Keywords: Crystal structure; diammonium hydrogentrisulfimide; IR spectrum; synthesis; thermal analysis

INTRODUCTION

The structure of the $N_3S_3O_6$ ring has been determined from single-crystal analyses for $Ag_3N_3S_3O_6{\cdot}3H_2O$,[1] ($\underline{N}$-$CH_3)_3N_3S_3O_6$,[2] ($\underline{O}$-$(CH_3)_3Si)_3N_3S_3O_6$,[3] and recently $(NH_4)_3N_3S_3O_6$[4,5] and has been found to vary depending on the various substituents and crystal interactions.[2,5] The variations in bond angles and lengths and deviation from planarity correlate with the expected amounts of electron density on the N's and, thus, on the extent of π-bonding in the N—S and S—O bonds. The $(\underline{N}—H)_3N_3S_3O_6$, which easily undergoes acid-catalyzed hydrolysis, has been prepared and partially characterized;[3] however, no crystal structure has been reported. Its reported aqueous pK's of 1.7, 2.1, and 4.4[3] suggest that the monoprotonated ring should be

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I thank Frederick Hollander, x-ray crystallographer at the University of California, Berkeley, for the single-crystal analysis and for his helpful suggestions.

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relatively unionized, less susceptible to cause self-acid-catalyzed hydrolysis, and thus, isolable as a salt by crystallization from aqueous solution. A single-crystal analysis of this salt would be of interest not only for being the first reported structure of a protonated $N_3S_3O_6$ ring, but also for structural correlations of the different sections of the unsymmetrical ring to the above compounds containing rings in symmetrical environments. Herein are reported the preparation and some properties of $(NH_4)_2HN_3S_3O_6$ and the X-ray structure of the $HN_3S_3O_6^{2-}$ ring.

RESULTS AND DISCUSSION

Syntheses

The synthesis of $(NH_4)_2HN_3S_3O_6$ involves an aqueous protonation reaction, Eq (1).

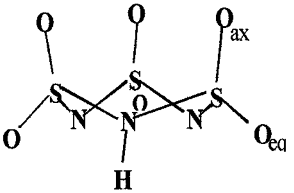
$$(NH_4)_3N_3S_3O_6 + HNO_3 \rightarrow (NH_4)_2HN_3S_3O_6 + NH_4NO_3 \qquad (1)$$

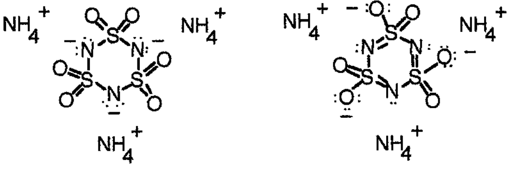
and the removal of NH_4NO_3 with ethanol. Because acid-catalyzed hydrolysis occurs readily, stoichiometric amounts of acid should be used along with rapid precipitation by adding ethanol. The powdery product is the hydrate, $(NH_4)_2HN_3S_3O_6 \cdot H_2O$, which dehydrates very slowly at about 19°C but rapidly at about 50°C. Crystallization by evaporation of water from an aqueous solution at 19°C or above gives the anhydrous salt, at 12°C or below gives the hydrated salt, and in between these temperatures gives a mixture. After dehydration, heating further produces a partial degradation of the ring at about 225°C, which probably involves the formation of $HN(SO_3NH_4)_2/NH_4N(SO_3NH_4)_2$, and a complete degradation to $(NH_4)_2SO_4$ starting at 250°C.[5]

Structure of the $HN_3S_3O_6{}^{2-}$ Ring

Due to instrumental limitations, the data for the large unit cell for the crystals of $(NH_4)_2HN_3S_3O_6$ were not sufficient for a complete crystal analysis, as discussed in the experimental section. However, the data were sufficient for refinement in a C-centered monoclinic subcell, where the positions of the hydrogen atoms in the ammonium ions are only averages and, thus, H-bonding involving the ammonium ions are not discussed, but the positions of the atoms in the $HN_3S_3O_6^{2-}$ rings are well defined and the various bond angles and lengths for the rings are accurate and are discussed below. Also, the subcell analysis indicates that there are hydrogen bonds between the H's on the rings and O's from neighboring rings connecting the slanted rings in chains.

In Table I the bond lengths and angles for the $HN_3S_3O_6^{2-}$ ion are listed. As shown, there are two types of O's, indicated as ax for axial and eq for equatorial. For comparison, geometrical data for other species containing the $N_3S_3O_6$ ring are also given. The range of S—N bond lengths reflect the bonding extremes for the $N_3S_3O_6$ ring as given by the two tautomeric forms.





($\underline{O}$-$(CH_3)_3Si)_3N_3S_3O_6$ with axial O's bonded to silyl groups would have the tautomeric form II and the shortest S—N bond, smallest <OSO angle, and largest <SNS angle. Even though the reported values were given without uncertainties and crystallographic data,[3] they correspond to those relatively expected for tautomeric form II. In contrast ($\underline{N}$—$CH_3)_3N_3S_3O_6$ with N's bonded to methyl groups would have the form I and, therefore, the longest S—N bond, largest <OSO angle, and smallest <SNS angle. The experimental values agree[2] except for the <SNS angle which is larger than expected though smaller than for ($\underline{O}$—$(CH_3)_3Si)_3N_3S_3O_6$. For the listed ionic compounds, $(NH_4)_3N_3S_3O_6$ with only hydrogen bonding between the NH_4^+ ions and the $N_3S_3O_6^{3-}$ ions[4,5] would have the most negatively-charged imido-N's and, thus, the most amount of electron density to transfer to the O's via the S's to form tautomeric form II. As one can see from the values in Table I, the transfer is not quite as complete as in ($\underline{O}$-$(CH_3)_3Si)_3N_3S_3O_6$ with silyl groups to decrease the buildup of charge on the O's and, thus, facilitate transfer. In $Ag_3N_3S_3O_6 \cdot 3H_2O$, the Ag^+ ions interact with the imido-N's with a bond order of 0.25 and are clearly aligned with the N's in the crystal structure.[1] This interaction decreases the amount of electron density on

TABLE I Average Bond Angles, °, and Lengths, Å, in the Ring for $(NH_4)_2HN_3S_3O_6$ and other Similar Compounds (Standard Deviations in Parentheses)

	S—N	S—O	<SNS	<NSN	<OSO	<NSO	<XNS
$(NH_4)_2HN_3S_3O_6$[a]	1.594 (7)	1.437 (6)eq	118.1 (5)	107.3 (3)	113.7 (2)	107.2 (8)eq	107 (4)
	1.690 (9)H[b]	1.446 (6)ax	115.7 (2)H		116.4 (2)H	112.8 (8)ax	X = H
						104.9 (3)H	
$(NH_4)_3N_3S_3O_6$[5]	1.604 (3)	1.447 (6)eq	117.5 (5)	109.2 (3)	113.1 (5)	106.6 (4)eq	
		1.469 (3)ax				110.6 (3)ax	
$(NH_4)_3N_3S_3O_6$[4]	1.599 (4)	1.448 (4)eq	118.4 (8)	109.2 (8)	111.7 (8)	107.0 (8)eq	
		1.459 (3)ax				110.8 (8)ax	
$Ag_3N_3S_3O_6 \cdot 3H_2O$[1]	1.636 (4)	1.436 (6)eq	115.0 (3)	106.1 (4)	117.4 (4)	106.2 (3)eq	
		1.456 (6)ax				110.1 (5)ax	
$(\underline{O}\text{-}(CH_3)_3Si)_3N_3S_3O_6$[3]	1.58	1.53eq	120	112	111		
		1.43ax					
$(\underline{N}\text{-}CH_3)_3N_3S_3O_6$[2]	1.669 (5)	1.409 (2)eq	117.1 (4)	104.5 (4)	121.9 (4)	106.6 (3)eq	117.3 (4)
		1.407 (2)ax				108.1 (2)ax	X = C

[a] H—N, 0.88 (6) Å.

[b] Section of the ring near the attached H atom.

the imido-N's and, thus, one would expect the ring in $Ag_3N_3S_3O_6 \cdot 3H_2O$ to be in between the two extremes. Indeed, the experimental bond length and angles indicate this. Clearly in $(NH_4)_2HN_3S_3O_6$ the ring is a composite of the two extremes. The side containing the N bonded to the H would be similar to $(\underline{N}\text{—}CH_3)_3N_3S_3O_6$, whereas the opposite side without the H would be similar to $(\underline{O}\text{-}(CH_3)_3Si)_3N_3S_3O_6$. The experimental values reflect these conclusions. In addition, the IR spectrum of $(NH_4)_2HN_3S_3O_6$ shows much more separation of the peaks in the $\nu(SO_2)_{sym}$ and $\nu(SO_2)_{asym}$ bands compared to the other compounds listed in Table I even though the average values of $\nu(SO_2)_{sym}$ and $\nu(SO_2)_{asym}$ have not changed significantly.[5] As mentioned above, the <SNS angle in $(\underline{N}\text{—}CH_3)_3N_3S_3O_6$ is not as small as expected from the trends of this angle for the other compounds. The steric hindrance of the CH_3-group increases the <CNS angle compared to the expected tetrahedral angle as shown by <HNS in $(NH_4)_2HN_3S_3O_6$. This not only affects the <SNS angle but decreases the differences between the <NSO angles and the S—O lengths compared to those in the other compounds.

Thus, the species containing the $N_3S_3O_6$ ring span the electronic arrangements from form I to form II with the unsymmetrical $HN_3S_3O_6^{2-}$ ion being a composite of both forms. The side of the ring containing the N bonded to H has form I whereas the side without the H has form II.

EXPERIMENTAL

The instruments and software are listed in Rustad.[5]

Syntheses of $(NH_4)_2HN_3S_3O_6 \cdot H_2O$ and $(NH_4)_2HN_3S_3O_6$

A powdered 1.03 g (3.57 mmol) sample of $(NH_4)_3N_3S_3O_6$[5] was dissolved in 1.49 mL of 2.40 M HNO_3 (3.58 mmol). Immediately, 95% ethanol was added to cause the formation of a voluminous, gelatinous, white precipitate. More ethanol was added (40 mL total) in order to stir and suction-filter the mixture. While still on the filter, the fine powder was washed twice with 30 mL of ethanol and twice with 15 mL of acetone, and then it was dried by passing air through it with suction until there was no further cooling of the glass filter due to the evaporation of the acetone. An immediate x-ray powder diffraction scan of the powder showed $(NH_4)_2HN_3S_3O_6 \cdot H_2O$ (see below) and a trace of $HN(SO_3NH_4)_2$ (PDF# 36-679). The mass and yield of the $(NH_4)_2HN_3S_3O_6 \cdot H_2O$ were 0.913 g and 88.3% respectively. An UV-VIS spectrum of an aqueous solution of a portion of the solid showed just an UV absorption edge starting at 240 nm and, thus, the absence of NO_3^- ions ($\lambda_{max} = 302$ nm).

The $(NH_4)_2HN_3S_3O_6{\cdot}H_2O$ was rapidly dehydrated at 50°C in a drying oven (30 min), giving $(NH_4)_2HN_3S_3O_6$ based on x-ray powder diffraction (see below). The hydrate loses water slowing at 20°C. Crystallization by evaporation of water from a saturated aqueous solution of $(NH_4)_2HN_3S_3O_6$ (solubility of 1.5 g/mL of water) at 12°C or less, at 19°C or above, or between 12 and 19°C produces crystals of $(NH_4)_2HN_3S_3O_6{\cdot}H_2O$, $(NH_4)_2HN_3S_3O_6$, or a mixture respectively. At higher temperatures and/or long evaporation times, hydrolysis tends to occur forming $HN(SO_3NH_4)_2$ and ultimately a mixture of $H_2NSO_2NH_2$, $(NH_4)_2SO_4$, and $(NH_4)_2(HSO_4)(H_2NSO_3)$ based on x-ray powder diffraction scans. An elemental analysis of recrystallized $(NH_4)_2HN_3S_3O_6$ gave caled (found): H, 3.34 (3.67); O, 35.38 (35.86); N, 25.81 (25.36); and S, 35.46 (35.06).

Stoichiometries

A 0.162 g (0.562 mmol) sample of $(NH_4)_3N_3S_3O_6$ was dissolved in 0.60 mL of 1.3 M HNO_3 (0.78 mmol). The liquid evaporated in less than a day, giving a crystalline residue of 0.200 g (calcd, 0.197 g, based on the complete reaction of $(NH_4)_3N_3S_3O_6$ to form a mixture of $(NH_4)_2HN_3S_3O_6$ and NH_4NO_3). The solid was pulverized, extracted with 2 mL of absolute ethanol, rinsed with two portions of 2 mL of acetone, air dried, and weighed. This was repeated four times until a constant mass of 0.152 g (calcd, 0.152 g, based on $(NH_4)_2HN_3S_3O_6$). The ethanol and acetone were evaporated from the combined extracts, leaving a solid residue of 0.043 g (calcd, 0.045 g, based on NH_4NO_3). X-ray powder diffraction scans of the two solids showed $(NH_4)_2HN_3S_3O_6$ with traces of hydrolysis impurities and NH_4NO_3 (PDF# 8-452), respectively. A UV-VIS spectrum of a solution of the $(NH_4)_2HN_3S_3O_6$ showed the absence of NO_3^- ions. Scaling up this procedure to prepare larger amounts of $(NH_4)_2HN_3S_3O_6$ was unsuccessful due to the longer evaporation times and greater amounts of hydrolytic impurities. A 0.1496 g sample of $(NH_4)_2HN_3S_3O_6{\cdot}H_2O$ prepared by recrystallization of $(NH_4)_2HN_3S_3O_6$ from aqueous solution at 12°C was heated at 58°C to a constant mass of 0.1402 g (calcd for $(NH_4)_2HN_3S_3O_6$, 0.1403 g).

Thermal Analysis and IR Spectra

A differential scanning calorimeter scan of $(NH_4)_2HN_3S_3O_6{\cdot}H_2O$ under nitrogen gas at 5°C/min showed medium endothermic peaks at 45–51 (integrated at 2°C/min, 40(4) kJ/mol) and 220–230°C and a large endothermic decomposition peak commencing at 250°C. The IR spectra of $(NH_4)_2HN_3S_3O_6{\cdot}H_2O$ and $(NH_4)_2HN_3S_3O_6$ are identical except for the

H_2O peaks. The spectral section from 3600–1400 cm^{-1} is a combination of the absorbances for NH_4^+ and/or H_2O taking into account the reduction of crystal site symmetry.[5,6] The remaining peak positions (cm^{-1}) are: 1369 m, sh to an NH_4^+ ion peak; 1312 vs; (1261 m, sh; 1240 s); 1182 s; (1122 vs; 1084 s, sh); 1005 s; 832 vs; 779 m, sh; 715 w; and 650 m.

Single-Crystal and X-ray Powder Diffraction

A fragment of a colorless, transparent crystal of $(NH_4)_2HN_3S_3O_6$ was used for the single-crystal analysis with a Siemens SMART diffractometer, see reference 5 for complete instrumental and software details. The observed reflections gave an apparent primitive monoclinic unit cell with 8 formula units. However, analysis of the structure of this cell yielded poor refinement and a clear indication of a $\underline{C}$-centered monoclinic subcell with a $\underline{b}$-axis of half the length of that of the primitive cell. Using a broader dynamic range CCD detector would produce more useful data to define the true larger unit cell. However, refinement of the data relative to this subcell converged rapidly with a significantly better R-value and approximately the same data/parameter ratio as for the larger cell. The subcell dimensions are given in Table II along with other crystallographic data.*

There were no differences in the locations of the atoms in the $HN_3S_3O_6^{2-}$ rings and of the nitrogen atoms in the NH_4^+ ions when the two refinements were compared. However, the refinement of the structure in the large cell with isotropic heavy atoms and group refinement of the NH_4^+ cations clearly showed visible differences in the hydrogen atom positions of the cations which were related by the 1/2* $\underline{B}$ translation and by the "$\underline{C}$-centering" translation. High correlation and low data/parameter ratio prevented further improvement of the refinement model for the large primitive cell. There was no indication for twinning of the smaller cell.

It seems clear that the large primitive cell is correct and that there is at least some ordering of the orientations of the ammonium cations on a periodicity of 26.18 Å. However, it is also clear that the resultant data are weak, fall off rapidly in $\sin\underline{\theta}/\underline{\lambda}$, and are insufficient to allow for the refinement of the structure in that cell. The refinement in the smaller $\underline{C}$-centered cell represents an averaging of the ammonium hydrogen positions, but it represents a good model for the geometry of the anion and the relationships of the same with the ammonium cations.

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*Crystallographic data have been deposited with the CCDC (12 Union Road, Cambridge CB2 1EZ, UK) and are available on request quoting the deposition number CCDC 185969.

TABLE II Single-Crystal Crystallographic Data for $(NH_4)_2HN_3S_3O_6$

fw, g/mol	271.29
Space group	Cc (#9), monoclinic
a/Å	7.318 (1)
b/Å	13.092 (4)
c/Å	9.441 (1)
β/deg	100.790 (1)
V/Å^3	888.5 (3)
Z	4
T/K	145 (1)
ρ_{calc}/gcm^{-3}	2.0281 (7)
F (000)	560.00
μ/cm^{-1} (Mo K_ω $\lambda = 0.71069$ Å, $3.00 < 2\theta < 45.00°$)	41.93
Crystal dimensions/mm^3	0.11 × 0.19 × 0.30, colorless
No. of reflections (unique, R_{int})	1925 (843, 0.017)
No. of observations ($I > 1.5\sigma(I)$)	711
No. of variables	141
R^a, R^b_w	0.021, 0.026
Maximal residual/eÅ^{-3}	0.17
Minimal residual/eÅ^{-3}	−0.22

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

$^bR_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ where $w = 1/(\sigma^2|F_o|)$.

The protonation of the ring clearly occurs on only one nitrogen site. When the model was refined without that hydrogen in place, the largest peak in the difference Fourier map occurred at that site. There were no peaks near the other two nitrogen atoms or near the oxygen atoms.

Due to the thermal expansion of the crystals, the room temperature (293 K) x-ray powder diffraction scan for $(NH_4)_2HN_3S_3O_6$ differs slightly from that predicted from the low temperature single-crystal results. The corresponding edge lengths and angles (a = 7.391(7) Å, b = 13.12(1) Å, c = 9.485(5) Å, β = 100.50(2)°) were determined from least-squares plots of the fundamental $1/d^2$ equation[7] for 39 indexed reflections, correlated with the single-crystal results based on the C-centered monoclinic subcell. The nonindexed powder diffraction data in d/Å (area %) for $(NH_4)_2HN_3S_3O_6 \cdot H_2O$ are the following: 11.2980 (28.4), 7.0262 (23.4), 6.6610 (100.0), 6.4766 (15.0), 6.3880 (32.6), 6.2557 (18.1), 5.6366 (15.0), 5.5400 (14.2), 5.3027 (78.3), 5.1281 (10.2), 4.8453 (32.3), 4.7327 (6.6), 4.3396 (14.1), 4.1517 (25.7), 4.0528 (7.5), 3.8484 (4.1), 3.8128 (1.2), 3.7487 (11.8), 3.6686 (11.0), 3.6312 (11.1), 3.5840 (7.5), 3.5245 (51.7), 3.3718 (16.7), 3.3259 (47.5), 3.2228 (11.7), 3.1797 (38.1), 3.1206 (72.4), 3.009 (1.7), 2.9506 (8.1), 2.8733 (1.0), 2.8205 (16.4), 2.7846 (4.9), 2.7674 (4.0), 2.7393 (10.7), 2.6472 (8.3), 2.6069 (15.0), 2.5583 (2.6), 2.5318 (1.2), 2.4997 (3.7), 2.4595 (9.9), 2.4322 (2.7), 2.3663 (8.1), 2.3094 (3.8), 2.2662 (2.5), 2.2387 (12.1), 2.2168 (2.0), 2.1602 (8.0), 2.1484 (10.0), and 2.0695 (9.5).

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