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Melemium Hydrogensulfate $H_3C_6N_7(NH_2)_3(HSO_4)_3$ – the First Triple Protonation of Melem

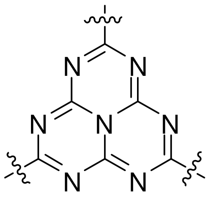
Andreas Sattler and Wolfgang Schnick*

Keywords: Heptazine; Tri-*s*-triazine; Crystal Structure.

We have synthesized melemium hydrogensulfate $H_3C_6N_7(NH_2)_3(HSO_4)_3$ by reaction of melem with 70 % sulfuric acid. The crystal structure was elucidated by single-crystal XRD ($P2_1/n$ (no. 14), $Z = 4$, $a = 10.277(2)$, $b = 14.921(3)$, $c = 11.771(2)$ Å, $\beta = 99.24(3)°$, $V = 1781.5(6)$ Å^3). $H_3C_6N_7(NH_2)_3(HSO_4)_3$ is the first compound displaying a triple protonation of melem. In this contribution an overview of accessible melemium sulfates depending on the concentration of sulfuric acid is given. Two additional melemium sulfates were identified this way.

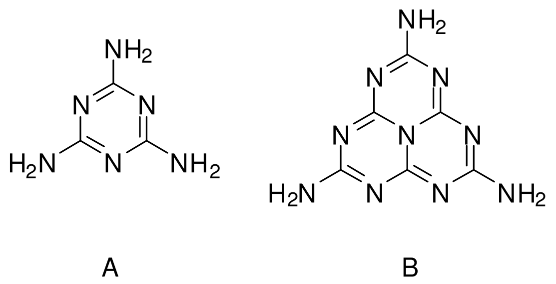
Introduction

The *s*-heptazine (tri-*s*-triazine, $[C_6N_7]$) core (cf. Scheme 1) constitutes a fundamental structural motif for carbon nitride materials. It is of considerable interest as a building block discussed for graphitic carbon nitride (g-C_3N_4) [1-3]. The heptazine core is also known as cyameluric nucleus, a name coined by Pauling [4] referring to cyameluric acid $H_3C_6N_7O_3$ [5]. Although much of the current interest concerning heptazines initially originated from the “harder than diamond” considerations based on calculations for certain modifications of C_3N_4 [6,7] additional properties (catalysis being a prominent example [3a,8,9]) have recently broadened the focus of carbon nitride chemistry.



Scheme 1. The cyameluric nucleus $[C_6N_7]$.

Typically, many heptazine-containing compounds are synthesized based on the thermal condensation of melamine (2,4,6-triamino-*s*-triazine, $C_3N_3(NH_2)_3$). The molecular compound melem (2,6,10-triamino-*s*-heptazine, $C_6N_7(NH_2)_3$, cf. Scheme 2) is a prominent example of a product obtained accordingly. Though known for a considerable period of time [10], melem has not been comprehensively characterized until very recently. Melem [11], some of its salts [12] and its molecular adducts with melamine [13] were thus discussed in prior investigations. We have found that melem can easily adopt different protonation grades (single and double protonation) in several compounds. So far, triple protonation of melem has not been observed in a crystalline compound.



Scheme 2. Structure of melamine $C_3N_3(NH_2)_3$ (A) and melem $C_6N_7(NH_2)_3$ (B).

In this contribution we report on the first example of a triple protonated $H_3C_6N_7(NH_2)_3^{3+}$ ion in the melemium hydrogensulfate salt $H_3C_6N_7(NH_2)_3(HSO_4)_3$. The compound was prepared by reaction of melem with 70 % sulfuric acid. We have investigated the structure and properties of this novel salt. Additionally, we present studies concerning the

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Table 1. Existence ranges of different melemium salts in relation to the concentration of sulfuric acid.

	Compounds observed as part of this work				
conc. (H_2SO_4) / wt %	0 - 0.04	7 - 40	44 - 48	53 - 58	>69
molarity (H_2SO_4) / mol l^{-1} [a]	0 - 0.4	0.78 - 4.9	5.6 - 6.3	7.2 - 8	>10
molality (H_2SO_4) / mol kg^{-1}	0 - 0.41	0.82 - 6.7	8.1 - 9.4	12 - 14	>23
observed compound [b]	melem hydrate	$H_2C_6N_7(NH_2)_3(SO_4) \cdot 2H_2O$	new salt A	new salt B	$H_3C_6N_7(NH_2)_3(HSO_4)_3$

[a] calculated neglecting excess volumes; [b] identified by XRD methods.

formation of different melemium sulfate salts depending on the respective concentration of sulfuric acid.

Results and Discussion

Different salts were observed upon subjecting melem to aqueous sulfuric acid solutions of various concentrations. This finding is in line with the observations made for the perchloric and methylsulfonic acid salts of melem, where a variety of salts has been found, as well [12]. While the concentration of the acid is a crucial factor, the amount of melem dissolved or suspended in the acid is only of minor importance. Values between 1 and 10 mg per mL of solution are suitable for lower sulfuric acid concentrations, while higher concentrations allow more melem to be used. As the concentration of H_2SO_4 rises the solubility of melem drastically increases. Melem also becomes prone to decomposition under these conditions. Complete decomposition requires boiling and rather long reaction times. This decomposition ultimately produces $(NH_4)_2SO_4$ and CO_2, however, intermediary occurrence of other compounds is to be expected.

We have characterized the salt $H_2C_6N_7(NH_2)_3(SO_4) \cdot 2H_2O$ [12a] in our previous investigations. The comprehensive study of the formation of melemium sulfate salts revealed a total of three new compounds (cf. Table 1). Starting from the concentrations known to produce $H_2C_6N_7(NH_2)_3(SO_4) \cdot 2H_2O$ [12a] we have identified new salts obtainable at higher concentrations of sulfuric acid. There, however, seem to be no additional salts that can be yielded at lower sulfuric acid concentrations. Instead the formation of melem hydrate [14] was observed for very dilute solutions. The list in Table 1 does not claim to be exhaustive since not all possible concentrations were investigated. Two of the three new salts discovered could unfortunately not be structurally studied as we have not succeeded in growing suitable single crystals. The third compound was yielded well-crystalline and could be investigated by single-crystal XRD. The formula was found to be $H_3C_6N_7(NH_2)_3(HSO_4)_3$, hence the compound is a triple-protonated melemium hydrogensulfate.

One might assume the acidity of $H_3C_6N_7(NH_2)_3^{3+}$ being higher than the one of HSO_4^- as no SO_4^{2-} is found in the compound. The pK_s value for HSO_4^- is given as 1.92 [15], the K_b values published for melem are $Kb_1 = 10^{-12}$, $Kb_2 = 6 \cdot 10^{-14}$, and $Kb_3 = 10^{-16}$ [16]. These values are supportive to this assumption, however, quite problematic, since solid-state and solution acidities usually differ and values are only applicable for very dilute solutions. Overall activity coefficients of H_2SO_4 in aqueous solution show a minimum for moderately concentrated solutions and rise by more than a magnitude (0.119 for c = 1 mol kg^{-1} to 1.701 for c = 20 mol kg^{-1} [17]) going from concentrations found to produce $H_2C_6N_7(NH_2)_3(SO_4) \cdot 2H_2O$ to the ones yielding $H_3C_6N_7(NH_2)_3(HSO_4)_3$ (cf. Table 1). The importance of SO_4^{2-} ions also diminishes in concentrated solutions. Solutions like those used for preparing compound A contain less than 1 % SO_4^{2-}, for the higher concentrated acids sulfate concentration is negligible [18]. The existence of the two other salts A and B suggests that triple protonation of melem might be possible at lower H_2SO_4 concentrations, as well and the compounds most likely incorporate the HSO_4^- ion.

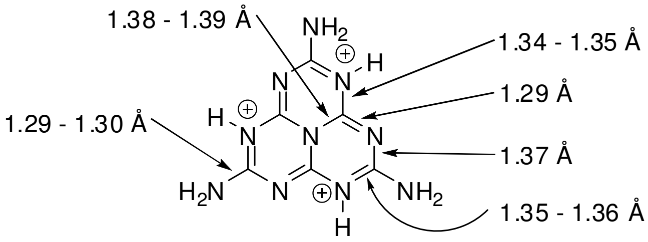
$H_3C_6N_7(NH_2)_3(HSO_4)_3$ is an extremely hygroscopic compound. Crystals of the title compound decay within split-seconds when subjected to moist air, thus the compound needs to be handled in an inert gas atmosphere. By reaction with moisture the compound is transformed into another melemium salt (a colorless solid) that, judging from powder XRD, is not identical with either one of the salts accessible from solution (cf. Table 1). After over-night exposure of $H_3C_6N_7(NH_2)_3(HSO_4)_3$ to air, elemental analysis data (cf. supporting information) suggests the uptake of 3–4 mole equivalents of water. Taking this properties into account, $H_3C_6N_7(NH_2)_3(HSO_4)_3$ might be used as desiccant or moisture sensor.

Table 2. Crystallographic data and details of the structure refinement for $H_3C_6N_7(NH_2)_3(HSO_4)_3$.

formula	$H_3C_6N_7(NH_2)_3(HSO_4)_3$	
formula weight / g mol^{-1}	512.44	
crystal system	monoclinic	
space group	$P2_1/n$ (no. 14)	
lattice parameters / Å, °	a = 10.277(2)	
	b = 14.921(3)	β = 99.24(3)
	c = 11.771(2)	
volume / $Å^3$	1781.5(6)	
Z	4	
diffractometer	Stoe IPDS	
radiation, monochromator	Mo-K_α (λ = 71.073 pm), graphite	
temperature / K	293	
structure solution	SHELXS [20] (direct methods)	
structure refinement	SHELXL [20] (full-matrix least-squares on F^2)	
corrections applied	Lorentz, polarization	
absorption coefficient / mm^{-1}	0.507	
calculated density / g cm^{-3}	1.911	
data / restraints / parameters	4087 / 0 / 328	
R-indices	R_1 = 0.0614 all data	
	R_1 = 0.0371 $F_o^2 > 2\sigma(F_o^2)$ (2894 reflections)	
	wR_2 = 0.0904 all data	
	wR_2 = 0.0851 $F_o^2 > 2\sigma(F_o^2)$	
GooF	0.947	
weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (0.0510P)^2$	
	where P = $(F_o^2 + 2F_c^2) / 3$	
largest peak / deepest hole / e $Å^{-3}$	0.367 / -0.393	

As mentioned above, the structure of the title compound was solved by single-crystal XRD (cf. Table 2).

$H_3C_6N_7(NH_2)_3(HSO_4)_3$ crystallizes in the monoclinic space group $P2_1/n$ with 4 formula units per unit cell. The asymmetric unit comprises one $H_3C_6N_7(NH_2)_3^{3+}$ ion and three hydrogensulfate ions. No solvate molecules are integrated into the compound.



Scheme 3. Bond lengths observed for the melemium ion found in $H_3C_6N_7(NH_2)_3(HSO_4)_3$.

The $H_3C_6N_7(NH_2)_3^{3+}$ ions display three protonation sites at the nitrogen atoms of the cyameluric nucleus. As expected the protons avoid close proximity, resulting in an arrangement closely resembling C_{3h} symmetry (cf. Scheme 3, Figure 1). The bond lengths within the heptazine core are notably affected by protonation (cf. Table 3). This is in accordance with observations for other melemium salts [12]. Bonds are influenced in a way that can best be described by assuming a slight preference for the resonance structure presented in Scheme 3. The C-N bonds to the amino groups are 2-3 pm shorter than the respective bonds in melem [11b].

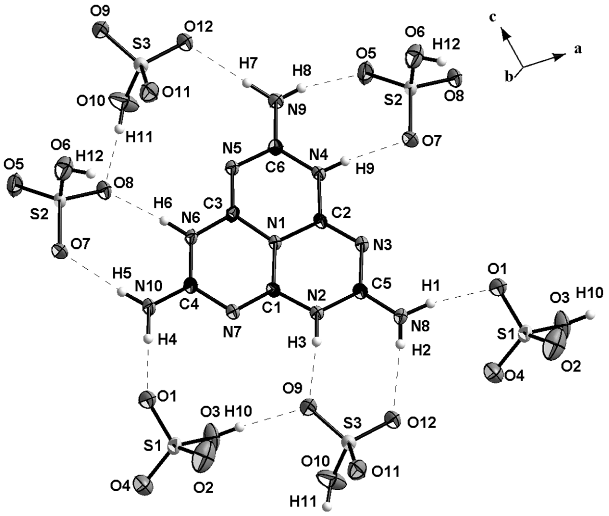


Figure 1. Molecular structure, H-bonding interactions and assignment of atom labels for $H_3C_6N_7(NH_2)_3(HSO_4)_3$. Ellipsoids drawn at the 50 % probability level.

The structure is stabilized by a multitude of H-bonding interactions. All possible NH and OH donors are involved in these interactions. The $H_3C_6N_7(NH_2)_3^{3+}$ ions are not linked to each other (cf. Figure 1) by H-bonding interactions due to steric and electrostatic reasons: The presence of three protonation sites at the cyameluric nucleus significantly limits the possibilities to establish favorable H-bonding motifs involving several bonds and H-bonding would require close proximity of two ions with a high positive charge.

Layer like H-bonded structures running perpendicular to *b* (cf. Figure 2) are assembled this way. The vast majority of H-bonds are located within the layers. Only some H-bonds are connecting two layers to each other forming a double-layer like arrangement (cf. Figure 3). H-bonds in $H_3C_6N_7(NH_2)_3(HSO_4)_3$ are found at D···A distances ranging from 2.62 to 2.98 Å and D-H···A angles between 154 and 175°. Thus the average distances are notably shorter than the ones observed for other melemium salts so far [12], allowing the conclusion that they are comparably strong. The IR spectrum of $H_3C_6N_7(NH_2)_3(HSO_4)_3$ (cf. Figure 3) shows a notable red-shift of the N-H and O-H bonds

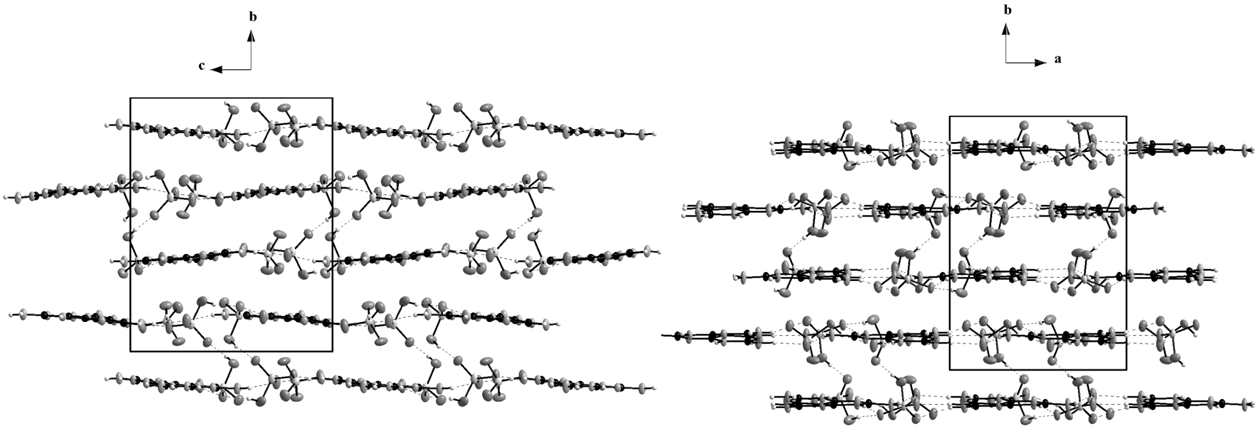


Figure 2. Layer-like arrangement of melemium ions in $H_3C_6N_7(NH_2)_3(HSO_4)_3$. Views along *a* (left) and *c* (right). Ellipsoids drawn at the 50 % probability level.

Table 3. Selected distances (in Å) and angles (in °) for $H_3C_6N_7(NH_2)_3(HSO_4)_3$. Standard deviations in parenthesis.

Distances				Angles					
C1-N7	1.294(3)	O1-S1	1.4629(18)	N7-C1-N2	120.6(2)	C1-N2-C5	122.38(19)	S1-O3-H10	101(3)
C1-N2	1.341(3)	O2-S1	1.425(2)	N7-C1-N1	123.48(19)	C1-N2-H3	118(2)	S2-O6-H12	107(3)
C1-N1	1.384(3)	O3-S1	1.5759(18)	N2-C1-N1	115.90(18)	C5-N2-H3	120(2)	S3-O10-H11	109(3)
C2-N3	1.290(3)	O3-H10	0.93(5)	N3-C2-N4	121.02(19)	C2-N3-C5	117.02(18)	O2-S1-O4	115.87(14)
C2-N4	1.350(3)	O4-S1	1.439(2)	N3-C2-N1	123.84(19)	C2-N4-C6	122.18(18)	O2-S1-O1	111.72(13)
C2-N1	1.391(3)	O5-S2	1.4322(17)	N4-C2-N1	115.14(18)	C2-N4-H9	115(2)	O4-S1-O1	111.45(11)
C3-N5	1.291(3)	O6-S2	1.536(2)	N5-C3-N6	120.93(18)	C6-N4-H9	123(2)	O2-S1-O3	106.28(12)
C3-N6	1.342(3)	O6-H12	0.81(4)	N5-C3-N1	123.56(19)	C3-N5-C6	117.14(18)	O4-S1-O3	104.29(12)
C3-N1	1.384(3)	O7-S2	1.4555(18)	N6-C3-N1	115.51(18)	C3-N6-C4	122.54(18)	O1-S1-O3	106.36(11)
C4-N10	1.299(3)	O8-S2	1.4673(17)	N10-C4-N7	118.9(2)	C3-N6-H6	116.9(19)	O5-S2-O7	113.24(11)
C4-N7	1.356(3)	O9-S3	1.4640(18)	N10-C4-N6	119.9(2)	C4-N6-H6	120.4(19)	O5-S2-O8	113.44(11)
C4-N6	1.367(3)	O10-S3	1.548(2)	N7-C4-N6	121.11(19)	C1-N7-C4	117.08(19)	O7-S2-O8	109.77(10)
C5-N8	1.291(3)	O10-H11	0.83(4)	N8-C5-N3	119.6(2)	C5-N8-H1	121.5(18)	O5-S2-O6	105.00(11)
C5-N3	1.353(3)	O11-S3	1.4450(19)	N8-C5-N2	119.1(2)	C5-N8-H2	122(2)	O7-S2-O6	107.56(13)
C5-N2	1.369(3)	O12-S3	1.4518(18)	N3-C5-N2	121.33(19)	H1-N8-H2	116(3)	O8-S2-O6	107.40(11)
C6-N9	1.302(3)	N8-H1	0.92(3)	N9-C6-N5	118.4(2)	C6-N9-H7	119.0(17)	O11-S3-O12	114.24(11)
C6-N5	1.350(3)	N8-H2	0.77(3)	N9-C6-N4	119.9(2)	C6-N9-H8	120(2)	O11-S3-O9	112.04(12)
C6-N4	1.369(3)	N9-H7	0.93(3)	N5-C6-N4	121.72(19)	H7-N9-H8	120(3)	O12-S3-O9	111.43(11)
N2-H3	0.81(3)	N9-H8	0.80(3)	C3-N1-C1	119.76(17)	C4-N10-H4	121(2)	O11-S3-O10	107.63(11)
N4-H9	0.81(3)	N10-H4	0.91(3)	C3-N1-C2	119.98(17)	C4-N10-H5	122.4(19)	O12-S3-O10	105.18(13)
N6-H6	0.86(3)	N10-H5	0.84(3)	C1-N1-C2	119.28(17)	H4-N10-H5	116(3)	O9-S3-O10	105.64(13)

supporting this assumption. Typical vibrations for N-C and S-O bonds were also found.

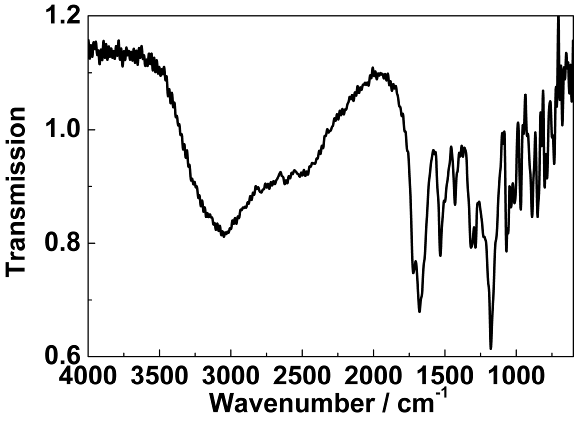


Figure 3. IR Spectrum (KBr) of $H_3C_6N_7(NH_2)_3(HSO_4)_3$.

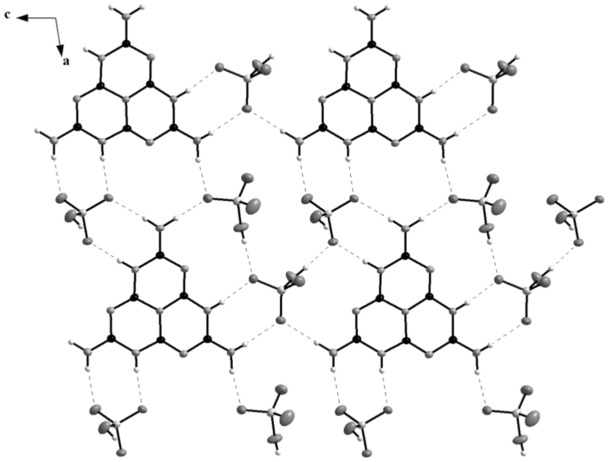


Figure 4. A H-bonded layer of melemium ions found in $H_3C_6N_7(NH_2)_3(HSO_4)_3$. View along *b*. Ellipsoids drawn at the 50 % probability level.

Similarly to $HC_6N_7(NH_2)_3H_2C_6N_7(NH_2)_3(SO_3Me)_3 \cdot H_2O$ and $H_2C_6N_7(NH_2)_3(SO_3Me)$, two melemium methylsulfonate salts which we described recently [12c], $H_3C_6N_7(NH_2)_3(HSO_4)_3$ also features short distances between S=O moieties and carbon or nitrogen atoms within the cyameluric nucleus. Especially the distances of the oxygen atom O2 to the atoms N1 (2.67 Å) and C2 (2.69 Å) are remarkably short (cf. Figure 1 for assignment). However, comparable distances are not unreasonable and have been reported in the literature [19]. Some examples even display notably shorter atomic distances. $H_3C_6N_7(NH_2)_3(HSO_4)_3$ shows the shortest such contacts yet found for melemium salts. This might be due to the higher positive charge of the $H_3C_6N_7(NH_2)_3^{3+}$ ion making interactions with negatively polarized oxygen atoms of the sulfate ions more favorable than has been the case in salts with lower protonation of melem.

$H_3C_6N_7(NH_2)_3(HSO_4)_3$ shows high thermal stability (cf. Figure 5). No thermal events were observed below 200 °C The endothermic event at 210 °C followed by a gradual weight loss can probably be explained by melting under decomposition. Another endothermic effect associated with a high weight loss is observed onsetting at 370 °C. Total decomposition is observed above 600 °C.

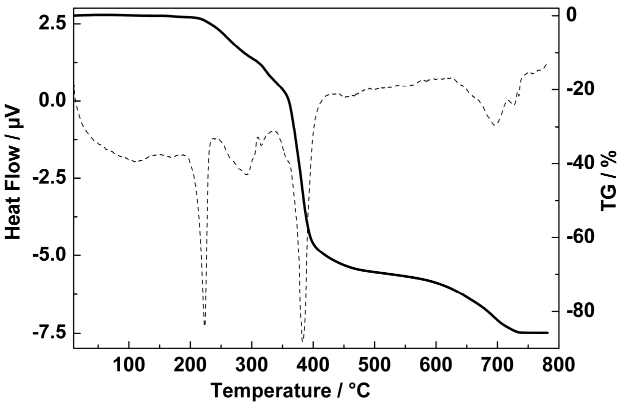


Figure 5. DTA/TG diagram of $H_3C_6N_7(NH_2)_3(HSO_4)_3$.

Conclusions

The structure of $H_3C_6N_7(NH_2)_3(HSO_4)_3$, the first triple-protonated melemium salt, was reported. The compound was yielded by crystallization from ca. 70 % aqueous sulfuric acid. The $H_3C_6N_7(NH_2)_3^{3+}$ ion was found to exhibit C_{3v} symmetry. The molecular structure of melem is characteristically affected by the protonation of the cyameluric nucleus. We have also investigated the stability of other melemium salts with respect to the concentration of sulfuric acid, showing the existence of two other salts the structure of which we, however, have yet not been able to elucidate.

Experimental Section

Single-crystal XRD: The crystal data of $H_3C_6N_7(NH_2)_3(HSO_4)_3$ was measured on a Stoe IPDS diffractometer. The measurement was conducted at a temperature of 293 K. The crystal structure was solved by direct methods (SHELXS-97) and refined against F^2 on all data by full-matrix-least-squares (SHELXL-97) [20]. Crystallographic data is summarized in Table 2. Selected distances and angles are presented in Table 3. Further details on the crystal structure can be obtained free of charge on application to Cambridge Crystallographic Data Centre (CCDC 768285), 12 Union Road, Cambridge CB2 1EZ (UK) (fax: +(44) 1223-336-033); e-mail **(fileserv@ccdc.cam.ac.uk)**.

PXRD diagrams were recorded on a Huber G670 Guinier Imaging Plate or a Stoe STADI P diffractometer. Measurements were conducted using monochromatic Cu-$K_{\alpha 1}$ radiation at room temperature

Thermal Analysis was performed using a Setaram TG-92 simultaneous thermal analyzer equipped with a protected (i.e. alumina covered) DTA/TG rod (P-type thermocouple, maximum operating temperature = 1600 °C). 22.5 mg $H_3C_6N_7(NH_2)_3(HSO_4)_3$ were heated to 800 °C in an atmosphere of streaming helium at a scanning rate of 10 K min^{-1} using a 100 µL alumina crucible.

FTIR measurements were conducted on an IFS 66v/S FTIR spectrometer (Bruker). KBr pellets were prepared in an argon glove box.

Melem: Melem was yielded by condensation of melamine in accordance to literature procedures [11,12c].

The title compound is very hygroscopic and rapidly decays when subjected to air. Isolation and all manipulations of $H_3C_6N_7(NH_2)_3(HSO_4)_3$ were thus carried out under dry argon using Schlenk techniques.

Melemium hydrogensulfate: Melem (4.2 g, 19.3 mmol) was dissolved in a hot mixture of conc. H_2SO_4 (35 mL) and water (15 mL). This needs to be conducted fast to avoid decomposition. The solution was stored at 4 °C over night. The colorless crystals were collected by filtration using a sintered glass frit washed twice with glacial acetic acid and dried at 10^{-3} mbar for at least 24 h. $H_3C_6N_7(NH_2)_3(HSO_4)_3$ was yielded as a colorless solid (3.89 g, 7.6 mmol, 39 %).

FTIR (KBr, 25 °C, cm^{-1}) 3040 s vbr, 1721 m, 1678 s, 1531 m, 1429 w, 1317 m, 1285 m, 1178 s br, 1068 m, 1037 w, 1012 w, 968 m, 889 m, 851 m, 801 w, 784 w, 734 w, 588 m, 572 s.

Crystals were selected in an argon glove box and measured in a sealed glass capillary.

Supporting information contains further experimental and analytical data for compounds A and B.

Acknowledgments

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Supporting Information:

Results and Discussion

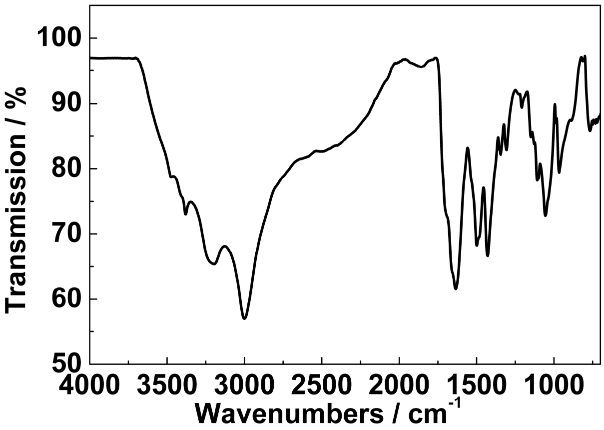

Figure S1. IR Spectrum (ATR, room temperature) of Compound A.

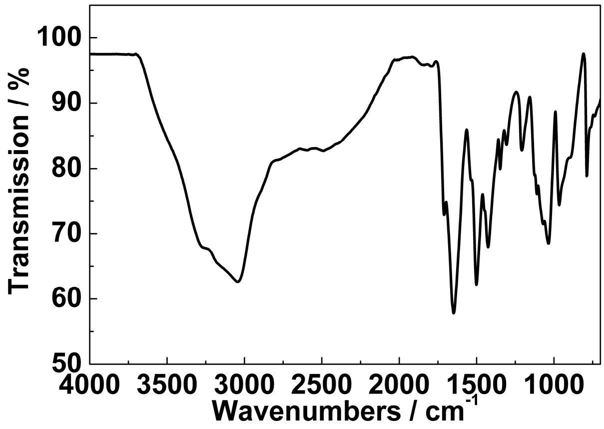

Figure S2. IR Spectrum (ATR, room temperature) of Compound B.

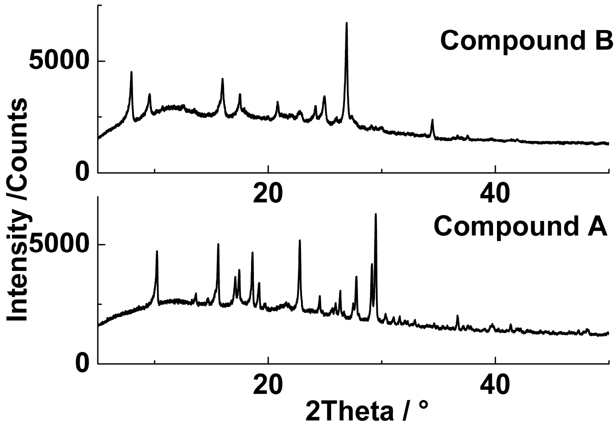

Figure S3. PXRD patterns (Cu$_{k\alpha1}$ Radiation) of compounds A and B.

Table S1. Elemental analysis for the decomposition product title compound after over-night exposure to air.

	C	N	H	S
found	11.27	21.65	3.63	16.13
calcd for $H_3C_6N_7(NH_2)_3(HSO_4)_3$	14.06	27.33	2.36	18.14
calcd for $H_3C_6N_7(NH_2)_3(HSO_4)_3 + 3H_2O$	11.96	23.25	3.68	15.97
calcd for $H_3C_6N_7(NH_2)_3(HSO_4)_3 + 4H_2O$	11.61	22.57	3.90	15.50

Experimental Section.

Compound A: Melem Melem (1.00 g, 4.587 mmol) was suspended in a hot solution prepared from water (30 ml) and H_2SO_4 (96%, 20 ml). The temperature was raised until all melem had dissolved. After cooling to 4 °C over night the colorless precipitate was collected by suction and dried on an absorptive piece of filter paper over night. Yield: 98 mg (percentages are not given since the formula of the compound is uncertain as of now).

Compound B: Melem (1.00 g, 4.587 mmol) was suspended in a hot solution prepared from water (35 ml) and H_2SO_4 (96%, 15 ml). The mixture was heated under reflux for approximately 10 min. Melem did not completely dissolve. After cooling to 4 °C over night the colorless precipitate was collected by suction and dried on an absorptive piece of filter paper over night. Yield: 921 mg (percentages are not given since the formula of the compound is uncertain as of now).