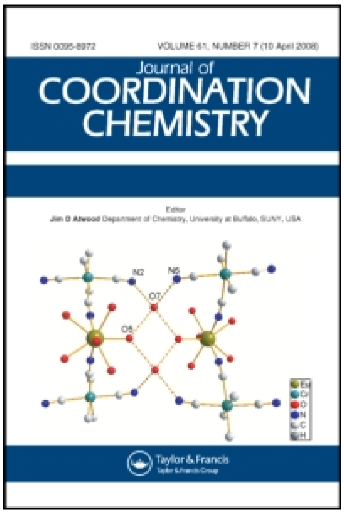

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
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Synthesis, spectroscopic characterization, and X-ray crystal structure of tris(trimethylsilyl)cyanurate

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To cite this Article El-Gamel, Nadia E. A. , Brand, Joerg and Kroke, Edwin(2009) 'Synthesis, spectroscopic characterization, and X-ray crystal structure of tris(trimethylsilyl)cyanurate', Journal of Coordination Chemistry, 62: 8, 1278 — 1284, First published on: 29 July 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970802499372

URL: http://dx.doi.org/10.1080/00958970802499372

Journal of Coordination Chemistry
Vol. 62, No. 8, 20 April 2009, 1278–1284

Synthesis, spectroscopic characterization, and X-ray crystal structure of tris(trimethylsilyl)cyanurate

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(*Received 5 June 2008; in final form 21 July 2008*)

Tris(trimethylsilyl)cyanurate, $C_{12}H_{27}N_3O_3Si_3$ (**1**), has been synthesized and characterized by elemental analysis, IR, Raman, ^{13}C and ^{29}Si NMR, and thermogravimetric methods. The molecular and crystal structure has been determined by single crystal X-ray diffraction. This compound crystallized in space group $P6_3/m$ (176), $Z = 2$ with $a = 11.017(2)$, $b = 11.017(2)$, $c = 9.676(3)$ Å; $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$. The geometry of the molecule is compared with tris(trimethylsilyl)cyamelurate.

Keywords: S-triazine; Tri-s-triazine; FTIR and Raman spectra; NMR; Thermal behavior; X-ray crystal structure

1. Introduction

1,3,5-Triazines and their substituted derivatives are heterocyclic analogs of benzene and substituted benzenes with aspects of structure and behavior which parallel those of other aromatic molecules [1]. These molecules and their derivatives show potential industrial [2] and pharmaceutical activities [3] and interesting electronic and optical properties. They have electron-transporting behavior and utilization in organic light-emitting diodes [4]. They also possess π-interaction abilities [5] and can be involved in intricate H-bond networks [6] for applications in organic [7] and supramolecular chemistry [8].

Many silicon-based polymers have proven to be promising precursors for fibers, adhesive, coating, and ceramic production. In the first half of the 19th century, the first synthesis of organosilicon compounds containing s-triazine derivatives were reported [9] with preliminary characterization using elemental analysis; potential applications of organosilicon-s-triazine have been reported [10].

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970802499372

Herein we report the molecular and the crystal structure of tris(trimethylsilyl)cyanurate, first reported in 1976 by reacting cyanuric acid with hexamethyldisilazane [11] characterized only by melting point and elemental analysis; in 1978 other authors prepared the same compound by silylation of cyanuric acid with trimethylsilylcyanide [12].

As s-triazine and tri-s-triazine derivatives attracted attention, tris(trimethylsilyl)cyanurate and its analog tris(trimethylsilyl)cyamelurate are used as precursors to synthesize versatile organic-inorganic hybrid polymers through sol-gel transitions [13].

In this article, the crystal structure of tris(trimethylsilyl)cyanurate is compared with its analog tris(trimethylsilyl)cyamelurate [14] and further physicochemical methods are used to characterize the title compound.

2. Experimental

2.1. *Materials*

All manipulations were performed under inert atmosphere using standard Schlenk techniques or in a nitrogen-filled glovebox. All chemicals were analytical grade and used without further purification, including cyanuric acid $C_3N_3O_3H_3$ (Fluka), 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (ABCR), and pentane (Merck).

2.2. *Synthesis of tris(trimethylsilyl)cyanurate; $C_3N_3(OSiMe_3)_3$*

Cyanuric acid (15 mmol, 2 g) and 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (24 mmol, 4 g) were mixed and heated in the presence of $(NH_4)_2SO_4$ as a catalyst for 12 h at 160°C under nitrogen. A white amorphous powder formed which was dried at 100°C under vacuum. Yield 98% (lit: 88.2%, [11, 12]). Colorless needles of the compound were isolated by recrystallization from pentane. m.p. 99–100°C (lit: 102–103°C, [12]). Elemental analysis results were as follows: C, 41.58%; H, 7.3%; N, 12.6%. Calculated for $C_{12}H_{27}N_3O_3Si_3$: C, 41.70%; H, 7.87%; N, 12.16%.

2.3. *Measurements*

Elemental analysis (C, H, N) was performed using a Foss Heraeus CHN-O-RAPID analyzer. FTIR spectra were recorded as KBr discs at room temperature by using a NICOLET 510 spectrometer from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1}. Raman spectra were obtained on a Bruker RFS 100/S module with a Nd : YAG laser ($\lambda = 1064$ nm) using aluminum capillaries of 2 mm diameter. The scanning ranges were 20–4000 cm^{-1} at 4 cm^{-1} resolution. TGA and DTA measurements were performed using Seiko Instrument S II TGA/DTA 22 : 10 mg was placed under nitrogen into an alumina crucible and heated to 1000°C (heating rate : 10°C min^{-1}) in an argon atmosphere. The ^{29}Si- and ^{13}C-NMR measurements were obtained on a Bruker Avance^{TM} 400 MHz with a resonance frequency of 79.51 MHz using magic-angle spinning (MAS) with a rotation frequency of 5000 Hz and with a cross polarization (CP) sequence.

2.4. *Crystal structure determination*

A suitable single crystal of **1** (approx. $0.5 \times 0.2 \times 0.1\,\mathrm{mm}^3$) was mounted under nitrogen on a glass fiber in an inert oil at 153(2) K. Exact cell dimensions were determined by refinement of the Bragg angles of 25 selected high-angle reflections from various parts of reciprocal space carefully centered on the diffractometer ($9.75 < \theta < 14.19$). Lp corrections and linear decay (−5.6%) corrections on the basis of three reflections measured every 60 min of X-ray exposure were applied. No absorption correction was applied. The respective $T_{\max}/T_{\min}$ value is contained in table 1. An Enraf-Nonius CAD 4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) was used. Full-matrix least-squares refinement was done on all unique F^2. Hydrogen atoms were inferred from neighboring sites and coordinates were refined freely with isotropic displacement parameters. Further crystal structure data are summarized in table 1. Programs used: ORTEP-III [15], SHELXS-97, SHELXL-97 [16] PLATON [17], and HELENA [18].

Table 1. Crystallographic data and structure refinement for tris(trimethylsilyl) cyanurate (**1**).

Chemical formula	$C_{12}H_{27}N_3O_3Si_3$
Chemical formula weight	345.64
Cell setting, space group	Hexagonal, $P6_3/m$
Unit cell dimensions (Å, °)	
a	11.017(2)
b	11.017(2)
c	9.676(3)
α	90
β	90
γ	120
Volume [Å^3]	1017.1(4)
Z	2
D_x (Mg m^{-3})	1.129
Radiation type	Mo-Kα
No. of reflection for cell Parameters	1532
θ range (°)	2.10–26.01
μ (Mo-Kα)(cm^{-1})	0.244
Crystal form, color	Needles, colorless
Crystal size (mm)	$0.48 \times 0.16 \times 0.12$
$F(000)$	372
Data collection	
$T_{\min}$	0.88
$T_{\max}$	0.97
R_{int}	0.0475
Range of h, k, l	$0 \rightarrow h \rightarrow 13$, $-13 \rightarrow k \rightarrow 0$, $0 \rightarrow l \rightarrow 11$
Refinement on	F^2
$R[F^2 \geq 2\sigma(F^2)]$, $wR(F^2)$, S	0.0350, 0.0789, 1.016
No. of reflections and parameters used in refinement	716, 45
H-atom treatment	Geom, refall
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (a{\cdot}P)^2 + b{\cdot}P]$ where $P = [\max(F_o^2, 0) + 2\,F_c^2]/3$
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.193, −0.237
Extinction method	SHELXS-97
Extinction correction	None

Computer programs used: ORTEP-III [15], SHELXS-97 [16a], SHELXL-97 [16b], PLATON [17] and HELENA [18].

3. Results and discussion

3.1. *Spectroscopic characterization*

FT-IR and Raman spectra of tris(trimethylsilyl)cyanurate presented in Supplemental Material reveal four characteristic absorption bands at 1703 (vs), 1544 (vs), 1397 (vs), and 841 (vs) cm^{-1} for triazine ring. Another band at 1133 (vs) cm^{-1} is attributed to Si-O-C units, the Si-CH_3 group is indicated by two characteristic bands at 1252 (vs) and 750 (vs) cm^{-1}, and two bands between 2963 (m) and 2901(m) cm^{-1} arises from symmetric and asymmetric CH_3 stretching vibrations, respectively. Raman spectrum shows characteristic vibrational bands at 1709 (m), 1545 (m), 1398 (m), and 837 (m) cm^{-1} corresponding to triazine ring, bands at 984 (m) and 635 (vs) cm^{-1} for Si-CH_3, and bands at 2962 (s) and 2903 (vs) cm^{-1} for symmetric and asymmetric CH_3 stretching vibrations, respectively.

The ^{13}C-NMR spectrum shows two bands, at 0.265 ppm attributed to CH_3 group, and downfield at 172 ppm assigned to OCN_2 of the triazine ring. ^{29}Si-NMR shows a single peak at 27.5 ppm due to $RSi(OMe_3)_3$ group.

3.2. *Thermogravimetric study*

The thermal stability of cyanurate was examined [19], and thermolysis of cyanurate salts were reported [20]. The thermogravimetric analysis of **1** is provided in Supplemental Material. The compound melts without decomposition at 100°C, as indicated by an endothermic DTA signal. At 200°C, sharp mass loss of 83.6% occurs, with an endothermic effect seen in the DTA curve; this loss can be related to condensation forming hexamethyldisiloxane $(CH_3)_3SiOSi(CH_3)_3$ and polymeric cyanuric acid anhydride $[C_3N_3O_{1.5}]_n$. A final broad step between 200°C and 340°C results in another 17% mass loss, with an endothermic signal at 336°C, characteristic for decomposition of s-triazine and/or the cyanurate $C_3N_3O_3$ units [20b–d].

3.3. *X-ray crystal structure*

The molecular structure of the title compound is shown in figure 1. Selected bond lengths and angles are listed in table 2. The ring system of the monocyclic anion $[C_3N_3O_3]^{3-}$ is exactly planar from delocalization of the π-electrons over the ring causing a rigid plane with D_{3h} symmetry. This was found in many sym-triazine derivatives like melamine $C_3N_3(NH_2)_3$ ring [5, 6] and some other s-triazine-based derivatives [21, 22].

The N–C bond lengths in the triazine ring range from 1.331(3) to 1.336(3) Å and the endocyclic angles at the N and C atoms are 112.8(3)° and 127.2(3)°, respectively; C-O bond lengths are 1.325(3) Å. There is a slightly distorted tetrahedral silicon, as observed for tris(trimethylsilyl)cyamelurate [14]. The angles are 112.02(9)° for C(3)–Si–C(2), 111.8(2)° for C(3)–Si–C(3), 109.89(8)° for O(1)–Si–C(3), 100.7(1)° for O(1)–Si–C(2) (table 2). Bond lengths of the three Si–CH_3 are almost identical (Si–C(3) 1.839(2) and Si–C(2) 1.844(3) Å). As the C-O bond lengths are equal, Si–O–C angles are 125.4(2)°. In tris(trimethylsilyl)cyamelurate the C–O bond lengths were 1.31(3) Å and Si–O–C angles ranged from 126.4(1)° to 127.2(1)°. Silicon atoms are located in the same plane as the $C_3N_3O_3$ units and all N–C–O–Si dihedral angles are exactly zero or 180° as reported for

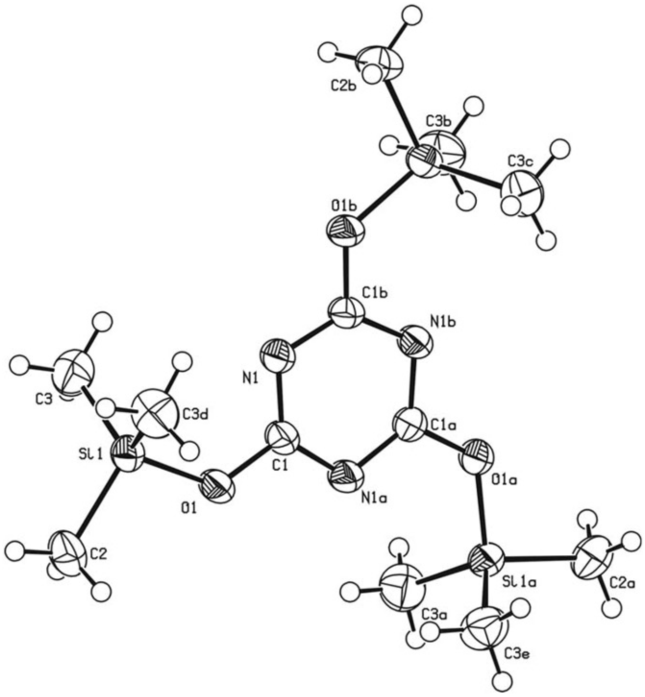

Figure 1. ORTEP drawing of tris (trimethylsilyl)cyanurate. Ellipsoids enclose 50% probability.

Table 2. Selected bond lengths (Å) and angles (deg) of tris(trimethylsilyl)cyanurate (**1**).

Si1–O1	1.695(2)
Si1–C3	1.839(2)
Si1–C3d	1.839(2)
Si1–C2	1.844(3)
O1–C1	1.325(3)
N1–C1	1.336(3)
N1–C1c	1.331(3)
C1–N1a	1.331(3)
O1–Si1–C3	109.89(8)
C3–Si1–C3d	111.8(2)
O1–Si1–C2	100.7(1)
C3–Si1–C2	112.02(9)
C3d–Si1–C2	112.02(9)
C1–O1–Si1	125.4(2)
C1c–N1–C1	112.8(3)
O1–C1–N1a	115.6(2)
O1–C1–N1	117.2(2)
N1a–C1–N1	127.2(3)

Symmetry transformations used to generate equivalent atoms: a: $-y$, $x-y$, z; c: $-x+y$, $-x$, $-z+0.5$; d: x, y, $-z+0.5$.

tris(trimethylsilyl)cyamelurate, but with dihedral angles less than 15°. Figure 2 presents the stacked layer; although there is a stacking interaction, no π–π interaction is found, as indicated by the relative large distance between these layers, 4.838(2) Å. In tris(trimethylsilyl)cyamelurate π–π interaction was found with distance of 3.515(2) Å,

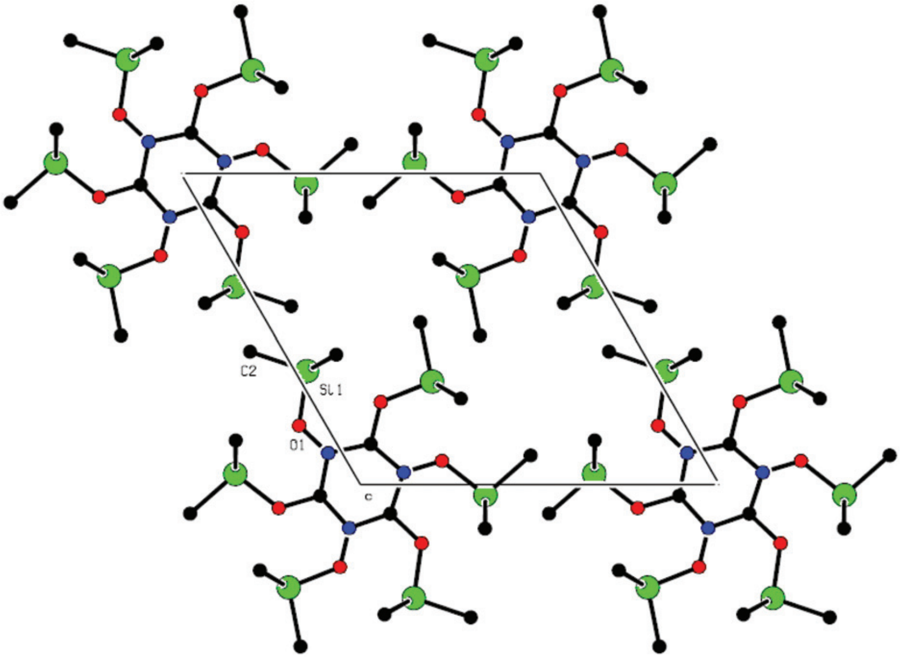

Figure 2. Projections of the unit cell contents onto the *ab* planes (PLATON [17]; H atoms are omitted for clarity).

close to the interlayer distance between π-stacked cyamelurate anions in alkali cyamelurates and bigger than the analogous distances in neutral compounds such as melem $[C_6N_7(NH_2)_3]$ [23], triazido-tri-s-triazine $[C_6N_7(N_3)_3]$ [24, 25], or trichloro-tri-s-triazine $(C_6N_7Cl_3)$ [26, 27].

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