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Crystal and molecular structure of Δ^6-5,6-diphenyl-5-methoxy-1,2,4-triazacyclohexene-3-thione and Δ^6-4-methyl-5,6-diphenyl-5-ethoxy-1,2,4-triazacyclohexene-3-thione

Elena Bermejo[a], Alfonso Castiñeiras[a], Douglas X. West[b,*]

[a]Departamento de Quimica Inorganica, Universidad de Santiago de Compostela, Santiago de Compostela, Spain
[b]Department of Chemistry, Illinois State University, Normal, IL 61790-4160, USA

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Abstract

Condensation of thiosemicarbazide or N(4)-ethylthiosemicarbazide with 1,2,8,9-tetraphenyl-3,7-diazanona-1,9-dione in the presence of copper(II) acetate in 96% ethanol leads to Δ^6-5,6-diphenyl-5-methoxy-1,2,4-triazacyclohexene-3-thione, $C_{16}H_{15}N_3OS$, or Δ^6-4-methyl-5,6-diphenyl-5-ethoxy-1,2,4-triazacyclohexene-3-thione, $C_{18}H_{19}N_3OS$. For $C_{16}H_{15}N_3OS$ the crystal data are monoclinic, $P2_1/c$, $a = 9.7780(7)$, $b = 8.5120(3)$, $c = 18.2210(13)$ Å, $\beta = 100.958(3)°$, $V = 1488.89(16)$ Å^3, and $Z = 4$ in agreement with an earlier report. For $C_{18}H_{19}N_3OS$ the crystal data are orthorhombic, $P2_12_12_1$, $a = 8.6940(3)$, $b = 12.9946(3)$, $c = 15.5139(5)$ Å, $V = 1752.68(9)$ Å^3, and $Z = 4$.

Keywords: Crystal structure; 1,2,4-Triazacyclohexene-3-thione; Thiosemicarbazide; Hydrogen bonding

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1. Introduction

Reports on the metal-induced cyclizations of various semicarbazones to 1,3,4-oxadiazole derivatives [1] and pyrazolonates complexes [2] have recently appeared. Potential cyclization products of thiosemicarbazones are 1,3,4-thiadiazoline-2-amines or 1,2-4-triazolidine-3-thione [2–4] if condensation takes place at the imine function. However, Δ^6-4-methyl-5,6-diphenyl-5-hydroxy-1,2,4-triazacyclohexene-3-thione, which forms a supramolecular structure via its intermolecular hydrogen bonds [5], results from condensation at an α-carbonyl position. Crystals of this compound were isolated from a preparative solution of 1,2,8,9-tetraphenyl-3,7-diazanona-1,9-dione (formed by condensation of 1,3-diaminopropane with benzil in a 1:2 molar ratio [6]), N(4)-methylthiosemicarbazide, and copper(II) acetate monohydrate in 96% EtOH. A similar reaction in which 3-piperidylthiosemicarbazide was used instead of N(4)-methylthiosemicarbazide produced the green, 4-coordinate copper(II) complex of benzil bis(3-piperidylthiosemicarbazone) [7]. In order to see whether a 1,2,4-azacyclohexene-3-thione with a supramolecular structure or a benzil bis(thiosemicarbazonato)copper(II) complex

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* Corresponding author. Address: Box 402, Long Beach, WA 98631, USA. Tel.: +1-360-642-5813.

E-mail address: westdx@hotmail.com (D.X. West).

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would be produced, we repeated the same reaction using thiosemicarbazide and N(4)-ethylthiosemicarbazide and report our results here.

2. Experimental

Equimolar (1 mmol) quantities of 1,2,8,9-tetraphenyl-3,7-diazanona-1,9-dione [5] and copper(II) acetate monohydrate (Fluka) in 25 ml of methanol were warmed until nearly complete dissolution was achieved. To this mixture solid thiosemicarbazide (Aldrich Chemical Company, Milwaukee, WI) or N(4)-ethylthiosemicarbazide (Aldrich) was added portion-wise over a period of 5 min, which resulted in some frothing, as well as immediate formation of a dark brown solid. The mixture was refluxed for an additional hour and a small amount of dark brown solid filtered from the mixture. The resulting filtrate was cooled and slow evaporation produced a larger amount of a yellowish solid in two days with crystals of diffraction quality.

2.1. X-ray data collection and reduction

A pale yellow prismatic crystal of Δ^6-5,6-diphenyl-5-methoxy-1,2,4-triazacyclohexene-3-thione, **1**, and Δ^6-4-methyl-5,6-diphenyl-5-ethoxy-1,2,4-triazacyclohexene-3-thione, **2**, were mounted on glass fibers and used for data collection. Cell constants and an orientation matrix for **2** by least-squares refinement of the diffraction data from 25 reflections in the range $21.27 < \theta < 42.97°$ with a Nonius CAD4 automatic diffractometer [8]. Data were collected for **1** at 294(2) K using Mo Kα radiation ($\lambda = 0.71070$ Å). Data were collected for **2** at 293(2) K using Cu Kα radiation ($\lambda = 1.54184$ Å) and the ω-scan technique and corrected for Lorentz and polarization effects [9].

2.2. Structure solution and refinement

The structures were solved by direct methods [10], which revealed the position of all non-hydrogen atoms, and refined on F^2 by full-matrix least-squares procedure using anisotropic displacement parameters [11]. The structure of **2** was refined as a racemic twin with components 0.52, 0.48(8) [12]. The hydrogen atoms attached to nitrogens were located from difference Fourier maps and refined isotropically while hydrogens attached to carbons were located in their calculated positions (C–H, 0.93–0.97 Å) and refined with a riding model. Atomic scattering factors were taken from the International Tables for Crystallography [13], and molecular graphics are from PLATON97 [14] and SCHAKAL [15]. A summary of the crystal data, experimental details and refinement results are listed in Table 1.

Table 1
Crystallographic data and methods of data collection, solution and refinement for Δ^6-4-methyl-5,6-diphenyl-5-ethoxy-1,2,4-triazacyclohexene-3-thione, **2**

Crystal data	**2**
Empirical formula	$C_{18}H_{19}N_3OS$
Crystal color, habit	Pale yellow, prism
Crystal size (mm)	0.40 × 0.30 × 0.30
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a, Å	8.6940(3)
b, Å	12.9946(3)
c, Å	15.5139(5)
Volume, $Å^3$	1752.68(9)
Z	4
Formula weight	325.42
Density (calcd), g/cm^3	1.233
Absorption coefficient, mm^{-1}	1.694
$F(000)$	688
Index ranges	$-10 \le h \le 0$
	$0 \le k \le 16$
	$-19 \le 1 \le 0$
θ range for data collection,°	4.44–74.61
Reflections collected	2053
Independent reflections, R_{int}	2053, 0.000
Data/restraints/parameters	2053/0/214
Absorption correction	ψ-scan
Max. and min. transmissions	0.978 and 0.929
Goodness-of-Fit	1.017
Largest diff. peak $eÅ^{-3}$	0.176
Largest diff. hole e $Å^{-3}$	−0.185
R_1, wR_2	0.0388, 0.0989
R_1, wR_2 (all reflections)	0.0586, 0.1091

3. Results and discussion

The structure of Δ^6-5,6-diphenyl-5-methoxy-1,2,4-triazacyclohexene-3-thione, **1**, has been reported in an earlier communication by reaction in the presence of HCl [4] rather than copper(II) acetate. The cell parameters, bond distances, angles and plane data we obtained for **1** are essentially the same as reported [4] and our data are included in the Tables for comparison purposes only. Table 2 lists the bond distances and angles for **1** and **2**, as well as for the previously reported Δ^6-4-methyl-5,6-diphenyl-5-hydroxy-1,2,4-triazacyclohexene-3-thione, **3**, [5] and Δ^6-4-amino-5,6-diphenyl-5-hydroxy-1,2,4-triazacyclohexene-3-thione, **4** **[16]**. The pathway of the reaction to form **3** likely proceeds by first condensation by the hydrazide nitrogen with one of the carbonyl groups [4] followed by reaction of the thioamide nitrogen with the other carbonyl to form the triazine ring and transfer of the proton to oxygen. Formation of **1** and **2** occurs in the same fashion (i.e. condensation between the hydrazide function and a carbonyl followed by interaction between the thioamide nitrogen and the second carbonyl for ring formation). However, a methyl group from a solvent molecule is found on oxygen in **1** instead of a hydrogen atom. In contrast, formation of **2** involves an ethyl group transferring to oxygen and a methyl group from solvent bonds to the substituting amide nitrogen atom. Therefore, rather than the hydrogen transferring to oxygen, the ethyl group moves. The replacement of the hydrogen of the thioamide function by a methyl group to form **2** probably occurs subsequent to ring formation.

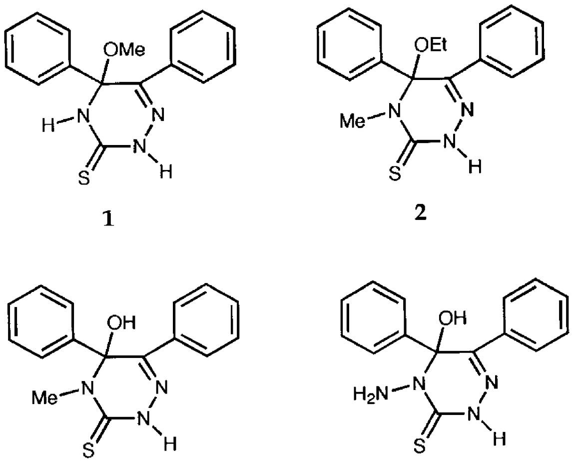
The O3–C30 bond distances in **1**, 1.437(3) Å and **2**, 1.444(4) Å, are essentially the same and the other important bond distances in compounds **1**–**4** are similar, except that C1–S1 is marginally shorter in **1** and **2**, Table 2. The C4–N5 bond distances of 1.290(3) and 1.286(4) Å in **1** and **2**, respectively, are consistent with a formal double bond as shown in Fig. 1. Since C1–N2, C1–N6 and N5–N6 are all in the 1.34–1.37 Å range, there is considerable delocalization of electron density about the ring. None of the angles in Table 2 for the four compounds show a significant difference. Therefore, the bond distances and angles of the 1,2,4-triazacyclohexene ring are not greatly affected by different substituents attached to the ring at least for these four compounds.

Intermolecular hydrogen bonding for **1** was not discussed in the previous communication concerning its structure [4]. Although the H6···S1 distances are comparable for the intermolecular

Table 2
Selected bond distances (Å) and angles (°) for Δ^6-5,6-diphenyl-5-methoxy-1,2,4-triazacyclohexene-3-thione, **1**, Δ^6-4-methyl-5,6-diphenyl-5-ethoxy-1,2,4-triazacyclohexene-3-thione, **2**, Δ^6-4-methyl-5,6-diphenyl-5-hydroxy-1,2,4-triazacyclohexene-3-thione, **3** and Δ^6-4-amino-5,6-diphenyl-5-hydroxy-1,2,4-triazaoyclohexene-3-thione, **4**

Bond	**1**	**2**	**3**	**4**
Cl–S1	1.673(2)	1.672(3)	1.697(2)	1.688(5)
C3–O3	1.414(2)	1.403(3)	1.405(2)	1.409(6)
C1–N2	1.335(2)	1.343(3)	1.336(2)	1.348(6)
N2–C3	1.460(3)	1.477(4)	1.481(2)	1.473(7)
C3–C4	1.528(3)	1.515(4)	1.517(3)	1.536(7)
C4–N5	1.290(3)	1.286(4)	1.281(3)	1.280(6)
N5–N6	1.367(3)	1.368(4)	1.369(2)	1.386(6)
N6–C1	1.345(3)	1.346(4)	1.347(3)	1.338(7)
Angle				
Cl–N2–C3	127.21(19)	125.0(3)	123.9(2)	124.5(5)
N6–N5–C4	118.95(18)	118.3(3)	117.3(2)	117.8(5)
N5–N6–C1	126.20(19)	127.0(3)	126.8(2)	125.5(4)
S1–C1–N2	124.45(17)	126.2(2)	123.6(2)	123.1(4)
S1–C1–N6	120.53(16)	118.2(2)	119.3(2)	120.3(4)
N2–C1–N6	115.0(2)	115.6(3)	117.1(2)	116.5(5)
O3–C3–N2	109.25(17)	109.1(2)	109.0(2)	110.2(4)
O3–C3–C4	111.55(18)	111.9(2)	111.0(2)	110.3(4)
N2–C3–C4	108.49(17)	109.9(2)	110.0(2)	107.5(4)
N5–C4–C3	123.4(2)	123.7(3)	124.9(2)	124.4(5)

Ref. [5]; Ref. [16].



1 **2**

3 **4**

Fig. 1. Representations of for Δ^6-5,6-diphenyl-5-methoxy-1,2,4-triazacyclohexene-3-thione, **1**, Δ^6-4-methyl-5,6-diphenyl-5-ethoxy-1,2,4-triazacyclohexene-3-thione, **2**, Δ^6-4-methyl-5,6-diphenyl-5-hydroxy-1,2,4-triazacyclohexene-3-thione, **3** and Δ^6-4-amino-5,6-diphenyl-5-hydroxy-1,2,4-triazaoyclohexene-3-thione, **4**.

Table 3
Hydrogen bonding interactions and mean plane data for **1** and **2**

Compound	D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠D–H···A (°)
1[a]	N2–H2···S1#1	0.82(2)	2.63(2)	3.427(2)	165(2)
	N6–H6···S1#2	0.94(2)	2.40(2)	3.308(2)	163(2)
	C30–H30···O3#3	0.96	2.60	3.431(3)	146
2[b]	N6–H6···S1#1	0.98(4)	2.43(4)	3.270(3)	143(3)
	Plane	Deviation	Atom, Largest deviation	Angle with previous plane	
1	N2–C1–N6–N5–C4–C3	0.0293	N2, 0.0489(0.0013)		
	C41–C42–C43–C44–C45–C46	0.0046	C41, 0.0073(0.0014)	36.27(0.07)	
	C31–C32–C33–C34–C35–C36	0.0031	C31, 0.0048(0.0014)		80.02(0.06)
2	N2–C1–N6–N5–C4–C3	0.0317	C3, 0.0499(0.0019)		
	C41–C42–C43–C44–C45–C46	0.0040		32.40(0.14)	
	C31–C32–C33–C34–C35–C36	0.0071		78.07(0.15)	

[a] #1: $-x, 0.5+y, 0.5-z$; #2: $-x, -0.5+y, 0.5-z$; #3: $-x, 1-y, -z$.

[b] #1: $0.5+x, 0.5-y, -1-z$.

hydrogen bond, N6–H6···S1, **1** has a longer N6···S1 distance and larger ∠N6–H6···S1 than **2**, Table 3. The second intermolecular hydrogen bond, N2–H2···S1, in **1** is somewhat weaker than N6–H6···S1 based on H···S and N···S distances. The N–H···S1 hydrogen bonding interaction in **3** [4], which in conjunction with the O–H···S interaction result in a supramolecular structure, is comparable to the hydrogen bonding parameters of **1** and **2**. For example, the non-bonding N···S distance is 3.3004(19) Å and ∠N6–H6···S1 is 158(2)°. This interaction in the three compounds has comparable parameters to those found for the much studied N-2-pyridyl-N′-arylthioureas [17]. A contribution to the intermolecular forces of **1** is an interaction between one of the hydrogen atoms in the methyl group and an O of a neighboring molecule O3; this interaction has similar parameters to the N2–H2···S1 interaction.

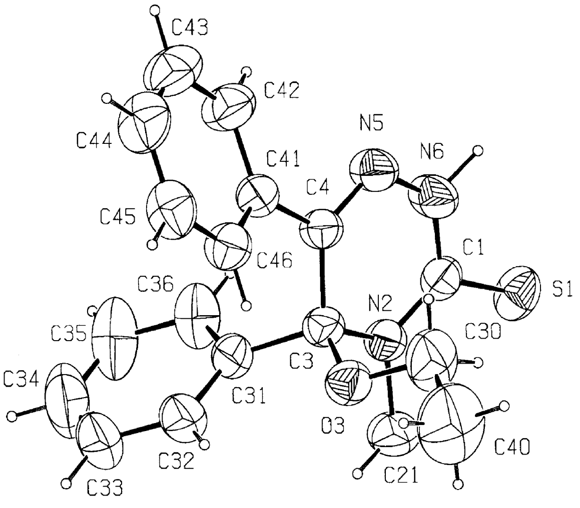


Fig. 2. ORTEP of Δ^6-4-methyl-5,6-diphenyl-5-ethoxy-1,2,4-triazacyclohexene-3-thione, **2**, with atom numbering scheme and displacement ellipsoids at 50% probability level.

The triazine ring is considerably less planar (mean plane deviation of 0.0293 and 0.0317 Å for **1** and **2**, respectively) than the two phenyl rings in the two compounds. This is in contrast to **3** in which the triazine ring has a similar planarity to the phenyl rings [5]. Among the six atoms in the triazine ring N2, C3 and N5 are most out of the plane for **1**, **2** (Fig. 2) and **3**, respectively. The angles between the mean planes of the phenyl rings and the triazine mean plane are listed in Table 3. The angle between the phenyl ring mean planes is 79.55 [4], 78.07(0.15) and 61.21(0.09)° for **1**, **2** and **3**.

4. Conclusion

Condensation of the thioamide nitrogen of the thiosemicarbazone moiety with an α-carbonyl function in the presence of copper acetate moiety produces a 1,2,4-triazacyclohexene-3-thione derivative unless the thioamide is tertiary [7]. The specific product of the cyclization is dependent on the thioamide substituents and the solvent used in the reaction. Therefore, this reaction might prove useful for the preparation of triazine ring compounds that are difficult to synthesize by other methods. Although **1**–**4** have different substituents, their bond distances and bond angles are similar indicating that the nature of substituent does not have a significant effect.

5. Supplementary material

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Center no CCDC-195702 for Δ^6-4-methyl-5,6-diphenyl-5-ethoxy-1,2,4-triazacyclohexene-3-thione, **2**. Copies of available data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-0-12-23-3-36-033; e-mail: for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

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