Synthesis, Crystal and Molecular Structure, and Spectroscopic Characterization of 5-(1-Hydroxycyclohexylthio)-1,3,4-thiadiazole-2-thione

Luciano Antolini, Andrea Cornia,* Antonio C. Fabretti and Luisa Schenetti
Dipartimento di Chimica Università di Modena, Via G. Campi, 183, 41100 Modena, Italy

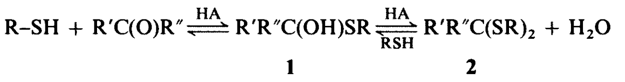
2,5-Dimercapto-1,3,4-thiadiazole (DMTDA), when dissolved in cyclohexanone, interacts strongly with the solvent and the title monothiohemiacetal (MTH) is formed. MTH has been characterized in the solid state by means of X-ray diffraction, IR spectroscopy and thermogravimetric analysis, and in cyclohexanone solution by means of NMR spectroscopy. The title compound crystallizes in the triclinic space group $P\bar{1}$ (No. 2), with cell dimensions a = 6.481(1), b = 9.322(1), c = 9.553(1) Å, α = 72.31(1), β = 89.74(1), γ = 80.83(1)° and Z = 2. The structure was solved by direct methods and least-squares refinement of structural parameters led to a conventional R factor of 0.041 for 1074 independent reflections. In the solid state, MTH easily undergoes decomposition with loss of cyclohexanone.

Cyclohexanone and other ketones are known to be particularly well-suited organic solvents for the extraction (preconcentration) of Cu^{II} from acidic aqueous solutions by 2,5-dimercapto-1,3,4-thiadiazole (DMTDA) derivatives and for the subsequent Cu^{II} Atomic Absorption determination.[1] This was generally ascribed to the good solvating properties of ketones, but the real nature of the interaction between the metal ion and the ligand in ketonic solution was unknown.

Even more striking results were found with palladium(II), whose complex with 3-(2-naphthyl)-DMTDA in acidic aqueous solution could be extracted by cyclohexanone only.[2]

Continuing our current interest in the complexing properties of polydentate heterocyclic ligands,[3] we focused our attention on the possible role of the solvent in determining the interactions between DMTDA and metal ions.

Thiols are actually known to be very reactive towards carbonyl compounds, affording dithioacetals (**2**) under acid catalysis according to Scheme 1.[4]



$$\text{R-SH} + \text{R}'\text{C(O)R}'' \underset{}{\overset{\text{HA}}{\rightleftharpoons}} \underset{\mathbf{1}}{\text{R}'\text{R}''\text{C(OH)SR}} \underset{\text{RSH}}{\overset{\text{HA}}{\rightleftharpoons}} \underset{\mathbf{2}}{\text{R}'\text{R}''\text{C(SR)}_2} + \text{H}_2\text{O}$$

Scheme 1

Monothiohemiacetals (**1**) are more stable than the corresponding hemiacetals obtained by nucleophilic addition of alcohols to aldehydes or ketones, and have often been isolated in a crystalline form.[5]

In the present paper we show that primary interactions between DMTDA and cyclohexanone occur both in the solid state and in cyclohexanone solution, and that the title monothiohemiacetal (MTH) is formed.

Results

The title compound was first obtained as a crystalline secondary product after precipitation of a Cu^{II}–DMTDA complex in cyclohexanone, an excess of DMTDA being present in the mother liquid. Subsequently, NMR spectroscopy showed that MTH formation was independent of the presence of the metal ion. Hence MTH was obtained directly by dissolving DMTDA in cyclohexanone, and was characterized in the solid state by X-ray diffraction, IR spectroscopy and thermogravimetric analysis (TGA).

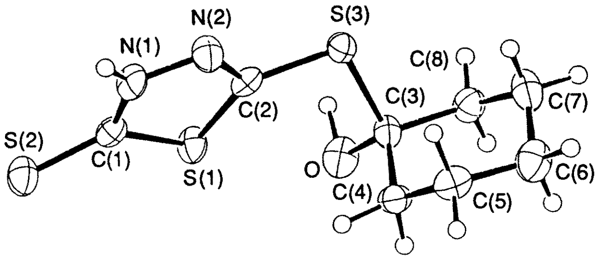


Fig. 1 ORTEP drawing of MTH with atom labelling scheme. Thermal ellipsoids for non-H atoms enclose 40% probability.

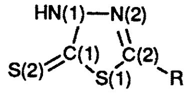


Fig. 2 Numbering scheme for 1,3,4-thiadiazole derivatives

Table 1 Bond distances (Å) and bond angles (°) involving non-hydrogen atoms

C(1)–S(1)	1.739(5)	C(2)–S(1)	1.742(5)
S(2)–C(1)	1.668(5)	N(1)–C(1)	1.321(6)
N(2)–N(1)	1.378(5)	C(2)–N(2)	1.292(6)
S(3)–C(2)	1.749(5)	C(3)–S(3)	1.863(5)
O–C(3)	1.418(5)	C(4)–C(3)	1.511(7)
C(8)–C(3)	1.530(6)	C(5)–C(4)	1.523(7)
C(6)–C(5)	1.515(7)	C(7)–C(6)	1.520(8)
C(8)–C(7)	1.516(7)		
C(2)–S(1)–C(1)	89.3(2)	S(2)–C(1)–S(1)	125.7(3)
N(1)–C(1)–S(1)	107.4(3)	N(1)–C(1)–S(2)	126.9(4)
N(2)–N(1)–C(1)	119.9(4)	C(2)–N(2)–N(1)	108.4(4)
N(2)–C(2)–S(1)	115.0(3)	S(3)–C(2)–S(1)	126.0(3)
S(3)–C(2)–N(2)	118.8(4)	C(3)–S(3)–C(2)	101.7(2)
O–C(3)–S(3)	109.5(3)	C(4)–C(3)–S(3)	111.8(3)
C(4)–C(3)–O	107.4(4)	C(8)–C(3)–S(3)	105.5(3)
C(8)–C(3)–O	111.6(4)	C(8)–C(3)–C(4)	111.1(4)
C(5)–C(4)–C(3)	113.0(4)	C(6)–C(5)–C(4)	110.6(4)
C(7)–C(6)–C(5)	110.7(5)	C(8)–C(7)–C(6)	110.3(4)
C(7)–C(8)–C(3)	113.8(4)		

Crystal Structure.—A drawing of the structure, showing the atom numbering scheme, is given in Fig. 1. Selected bond distances and angles are reported in Table 1. For the sake of easier comparison, some relevant bond distances observed in other 1,3,4-thiadiazole derivatives are summarized in Table 2 (see Fig. 2).

Table 2 Summary of bond distances (Å) in some 1,3,4-thiadiazole derivatives (see Fig. 2)

	R				
Bond	-S-CH_3	-SH	-NH_2	-S-$C_2HN_2S_3$	-S-$C_6H_{11}O$
C(1)-S(2)	1.665(4)	1.669(2)	1.678(7)	1.67-1.64[a]	1.668(5)
C(2)-R	1.730(4)	1.743(2)	1.339(9)		1.749(5)
N(1)-N(2)	1.381(4)	1.366(2)	1.382(8)		1.378(5)
C(1)-N(1)	1.330(5)	1.338(2)	1.334(9)	1.34-1.35[a]	1.321(6)
C(2)-N(2)	1.282(5)	1.296(2)	1.305(6)	1.25-1.29[a]	1.292(6)
C(1)-S(1)	1.738(4)	1.740(2)	1.738(5)		1.739(5)
C(2)-S(1)	1.744(4)	1.736(2)	1.746(7)		1.742(5)
Ref.	5	6	7	8	This work

[a] The two thiadiazole rings have slightly different geometries.

Table 3 ^{13}C δ values (ppm) for solutions of DMTDA in cyclohexanone (referred to TMS)[a]

MTH[b]	C(1)	C(2)	C(3)	C(4), C(8)	C(5), C(7)	C(6)
	154.9	190.7	90.8	39.6	hidden	23.3
Cyclohexanone			C=O	C_α	C_β	C_γ
			211.4	41.1	27.2	25.2

[a] Corresponding MTH and cyclohexanone carbon atoms are in the same column. [b] The crystallographic atom numbering scheme is followed (Fig. 1).

The thiadiazole ring is almost planar. The largest torsion angle within the five-membered ring is −2.4(6)°, and the maximum atomic deviation from the least-squares mean plane is −0.012 Å.

Interatomic distances follow the same pattern previously observed for the thione–thiol tautomeric form of simple DMTDA derivatives: one of the exocyclic C–S bond lengths [C(1)–S(2), 1.668(5) Å] is significantly shorter than the other [C(2)–S(3), 1.749(5) Å], suggesting different amounts of double bond character in these two bonds. Correspondingly, the two cyclic C–N bond lengths are markedly different, C(2)–N(2) [1.292(6) Å] being an almost pure double bond.

Similar results were obtained for 2-mercapto-5-methylthio-1,3,4-thiadiazole,[6] 2,5-dimercapto-1,3,4-thiadiazole (DMTDA),[7] 5-amino-2-mercapto-1,3,4-thiadiazole[8] and 5,5′-dimercapto-bis(1,3,4-thiadiazol-2-yl)disulfide (Table 2),[9] while completely different geometries were observed for DMTDA derivatives in the thiol–thiol tautomeric form.[10]

Except for the rather short N(1)–N(2) bond of 1.366(2) Å in DMTDA, which was attributed to intermolecular hydrogen bonding involving N(2),[6] all the reported interatomic distances seem to be only slightly influenced by the nature of R, the geometry of the ring being largely determined by N(1) protonation and by the quite large double bond character of the C(1)–S(2) bond.[11,12]

The geometry of the N–C=S group is very similar to that observed in non-cyclic thioamides.[13] However, the C(2)–R bond length shows that resonance between R and the ring is also possible.

C(3)–O [1.418(5) Å] can be considered as a pure single bond.[13]

The cyclohexane ring has the classical chair conformation, C(3)–S(3) being an axial bond.

No appreciable interaction between the partial negative charge on oxygen and the slightly positive S(1)[11] seems to occur, since the C(2)–S(3)–C(3) angle [101.7(2)°] is close to the value observed for 5-methylthio-1,3,4-thiadiazole-2-thione [100.1(2)°].[6]

There is agreement between N(2)–N(1)–C(1) and C(2)–N(2)–N(1) angles [119.9(4)° and 108.4(4)°, respectively] and the position of hydrogen on N(1).[14] Similar results were found for 2-mercapto-5-methylthio-1,3,4-thiadiazole,[6] 2,5-dimercapto-1,3,4-thiadiazole (DMTDA),[7] 5-amino-2-mercapto-1,3,4-thiadiazole[8] and for an *N*-methyl-1,3,4-thiadiazole mesoionic derivative.[15]

The crystal packing is mainly determined by two intermolecular hydrogen bonding interactions. The stronger one occurs between the N–H ring group and the S(2) atom [N(1) ··· S(2) = 3.326(4) Å; ∠N–H ··· S = 175°]. The weaker contact involves the OH function and again the S(2) atom [O ··· S(2) = 3.418(4) Å; ∠O–H ··· S = 166°]. Furthermore, there is one very short van der Waals contact between O atoms with an interatomic separation of 3.073(7) Å.

NMR Results.—We have performed a ^{13}C NMR study of the yellow solution obtained by dissolving DMTDA in cyclohexanone under gentle heating (DMTDA : cyclohexanone mole ratio 1 : 6).

The ^{13}C {^1H}-decoupled NMR spectra were performed with a standard pulse sequence at 313 K. The ^{13}C δ values and the peak assignments are reported in Table 3. The signal at 90.8 ppm is considered indicative of the presence of MTH, no signals arising from DMTDA or cyclohexanone being expected in this region, and its position is consistent with C(3) having monothiohemiacetalic character.

In the range 0–50 ppm, three inequivalent carbon atoms of the MTH cyclohexyl moiety are detected, the fourth probably being hidden by the strong cyclohexanone signal at 25.2 ppm. As compared to free cyclohexanone, all the cyclohexyl ring carbon atoms in MTH, except for C(3), appear to be slightly shielded.

In the range 100–200 ppm, where the thiadiazole signals are expected, two peaks are detected at 154.9 and 190.7 ppm. To our knowledge, no DMTDA ^{13}C data have been previously reported and we could not succeed in obtaining a ^{13}C spectrum of DMTDA in standard NMR solvents because of the very low solubility of DMTDA. However, NMR data on closely related molecules[16] allowed unambiguous assignment of the 154.9 ppm signal to the thione carbon atom C(1). Consequently, the 190.7 ppm signal was assigned to the C(2) carbon atom. The intensities of the signals at 90.8, 154.9 and 190.7 ppm are approximately equal. The relative intensity of the recorded peaks was unchanged 24 h after sample preparation.

MTH signals cannot be observed either in $CDCl_3$ solutions of DMTDA and cyclohexanone, for DMTDA : cyclohexanone mole ratios ranging from 1 : 1 up to 1 : 10, or on dissolving solid MTH in $CDCl_3$.

IR Results.—The solid state IR spectrum of MTH shows medium strong absorptions at 3380 and 3060 cm^{-1} which may be assigned to associated O–H and associated N–H stretching modes, respectively.[9,17]

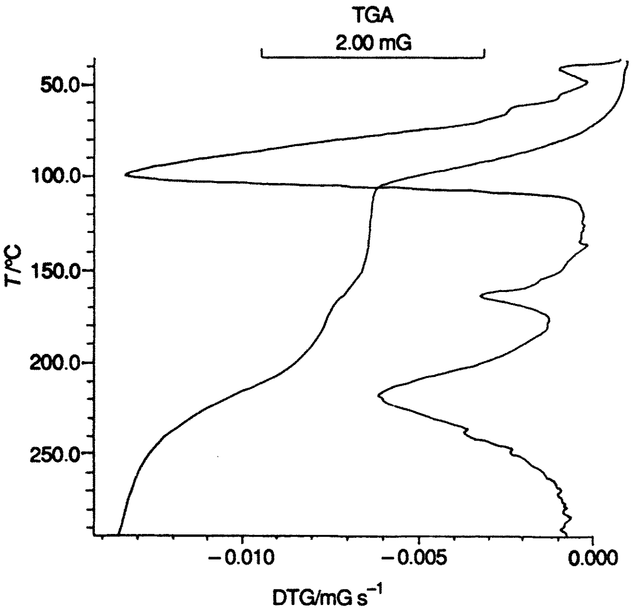


Fig. 3 TGA diagram of MTH

Table 4 Observed percentage weight losses in MTH thermogravimetric analysis

Step no.	T interval/°C	Observed weight loss (%)
1	37.6–135.6	40.27
2	135.6–177.0	6.44
3	177.0–283.6	31.44

Only a very weak ν(C=O) absorption appears at 1710 cm^{-1}, and this may be attributed to partial MTH decomposition and/or slight solvent inclusion, since it was not observed in freshly prepared, carefully washed samples.

In the IR spectrum of thioamides four strong bands, called THIOAMIDE I, II, III and IV and arising from mixed contributions of δ(N–H), δ(C–H), ν(C–N) and ν(C=S) are usually observed at *ca.* 1500, 1300–1200, *ca.* 1000 and 850–700 cm^{-1}.[18,19] In solid MTH strong thioamidic bands are observed at 1494 (THIOAMIDE I), 1276 (THIOAMIDE II), 1117/1058 (THIOAMIDE III) and 768 (THIOAMIDE IV) cm^{-1},[9] while the 718 (s) cm^{-1} band may be assigned to a C–S(endocyclic) stretching mode.[17]

Aliphatic C–H stretching bands are observed at 2950–2910 cm^{-1}. Other very sharp bands, probably due to cyclohexyl moiety vibrations, are present.

Solutions of solid MTH in CH_2Cl_2, $CHCl_3$ and CCl_4 show strong absorption bands at 1710 cm^{-1}, this being good evidence for MTH decomposition.

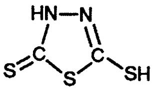
When strong cyclohexanone absorptions are subtracted, the liquid-film IR spectrum of MTH crystals' mother liquid resembles that of solid MTH, except for a slight hypsochromic shift and broadening of the N–H stretching band (3110 cm^{-1}) and for the very broad profile which can be observed at 3400 cm^{-1}. In particular, the two spectra are identical in the 2600–2300 cm^{-1} region, no S–H stretching band being present.

TGA Results.—In Fig. 3 and in Table 4 we report a TGA diagram and the observed percentage weight losses, respectively. Step 1 can be ascribed to quantitative cyclohexanone loss (required loss: 39.51%). Steps 2 and 3 are probably due to sulfide formation with H_2S loss (required loss: 6.91%) and to the subsequent decomposition of the rings, respectively. In fact, when subjected to prolonged heating in alcohol or water, DMTDA is known to afford 5,5′-dimercapto-bis(1,3,4-thiadiazol-2-yl)sulfide (yellow crystals), which melts with decomposition at 178 °C.[20] There is excellent agreement between this data and the start temperature of the third step (177.0 °C).

Discussion

One of the most interesting properties of DMTDA is its possible existence[21] in the thione–thiol (**4**) and thione–thione (**5**) tautomeric forms. In the solid state, DMTDA is actually present as the thione–thiol tautomer,[7] while in solution a solvent-dependent equilibrium is believed to exist[22] between the thione–thiol (**4**) and thione–thione (**5**) forms, the former being the prevailing species in benzene, chloroform, ethanol and dimethylformamide. In particular, the IR spectrum of chloroform solutions of DMTDA show both strong thioamidic absorptions and a sharp S–H stretching band at 2570–2560(w) cm^{-1}. However liquid-film IR spectra of saturated solutions of DMTDA in cyclohexanone show no ν(S–H) band, this being good evidence that in cyclohexanone solution MTH exists in the same tautomeric form as in the solid state (thione form) and that free DMTDA, if present exists as the thione–thione tautomer (**5**).

Though the free thione–thione DMTDA ^{13}C signal might coincide with the C(1) peak at 154.9 ppm, the sharpness and relative intensities of NMR signals at 190.7, 154.9 and 90.8 ppm suggest that MTH is likely to be the prevailing species in cyclohexanone solutions of DMTDA.



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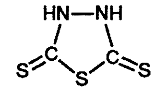

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On the other hand, both NMR and IR results indicate that MTH is not formed to an appreciable extent from DMTDA and cyclohexanone in inert solvents (CH_2Cl_2, $CHCl_3$ and CCl_4).

As shown by TGA results, MTH is subject to easy decomposition in the solid state, with cyclohexanone evolution.

Conclusions

The solid state structure and characterization of 5-(1-hydroxycyclohexylthio)-1,3,4-thiadiazole-2-thione (MTH), a novel monothiohemiacetal which is formed in cyclohexanone solutions of 2,5-dimercapto-1,3,4-thiadiazole (DMTDA), has been reported. An attempt to reveal MTH in inert solvents (CH_2Cl_2, $CHCl_3$ and CCl_4) was unsuccessful.

On the basis of such strong interactions between DMTDA and cyclohexanone, the usual solvation models[1,2] may be inadequate when an explanation of the complexing properties of DMTDA derivatives towards metal ions in cyclohexanone is required.

Experimental

All the chemicals were Reagent Grade and used as received.

DMTDA (Lancaster Synthesis) (0.5 g; 3.3 mmol) was dissolved in cyclohexanone (Merck) (1.0 cm^3; 9.6 mmol) and diethyl ether (5 cm^3) under gentle heating. The solution was filtered and allowed to slowly lose diethyl ether by standing at room temperature. After 14 h, it afforded extensively geminate, air-sensitive, colourless crystals which, after filtration, were rapidly washed with light petroleum (35–60 °C) and dried (0.2 g, 24%).

When slowly heated in a melting-point apparatus, the crystals under study at first lost cyclohexanone which condensed on the colder internal walls of the glass capillary; then, over a wide temperature interval (100–140 °C), they progressively disappeared affording a yellow liquid which finally decomposed at 140–145 °C with H_2S evolution (Found: C, 37.4; H, 5.2; N, 11.2; S, 38.65. $C_8H_{12}N_2OS_3$ requires: C, 38.68; H, 4.87; N, 11.28; S, 38.73%).

Crystal Data.—$C_8H_{12}N_2OS_3$, $M = 248.38$, triclinic, $a = 6.481(1)$, $b = 9.322(1)$, $c = 9.553(1)$ Å, $\alpha = 72.31(1)$, $\beta = 89.74(1)$, $\gamma = 80.83(1)°$, $V = 542(1)$ Å^3 (by least-squares refinement on diffractometer angles of 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P\bar{1}$ (No. 2), $Z = 2$, $D_x = 1.52$ g cm^{-3}, $F(000) = 260$. Colourless, air sensitive tablets. Crystal dimensions 0.24 × 0.18 × 0.14 mm, μ(Mo-Kα) = 5.8 cm^{-1}.

Data Collection and Processing.—CAD4 diffractometer, ω–2θ mode with ω scan width = $(0.75 + 0.35 \tan \theta)$, ω scan speed 1.0–2.7° min^{-1}, graphite-monochromated Mo-Kα radiation. Of 2509 measured reflections ($1.5 \le \theta \le 27°$), 1160 had $I > 3\sigma(I)$, and 1074 were independent ($R_{\text{int}} = 1.9\%$) and were used in the structure analysis.

Linear and approximate isotropic crystal decay, *ca.* 61.6% during 34.5 h of exposure time, corrected during processing. Absorption correction was not applied.

Structure Analysis and Refinement.—Direct methods (SHELX 86[23]) and full-matrix least-squares (SHELX 76[24]). All non-hydrogen atoms anisotropic; hydrogen atoms located in ΔF maps, refined isotropically through some least-squares cycles and then held fixed because of the low reflection/parameter ratio. The weighting scheme $1.45/[\sigma^2(F_0) + 0.000\,37\,F_0{}^2]$, with $\sigma(F_0)$ from counting statistics, gave satisfactory agreement analyses. Final R and R' values were 0.041 and 0.040. No evidence for secondary extinction.

Scattering factors were from SHELX 76.[24] All calculations carried out on a VAX 6310 computer. Full lists of atomic temperature factors, positional and thermal parameters, bond distances and angles involving H atoms, short van der Waals contacts, torsion angles and selected least-squares planes have been deposited at the Cambridge Crystallographic Data Centre.*

NMR Spectra.—The ^{13}C spectra were recorded at 100.61 MHz on a Bruker AMX-400 Spectrometer using D_2O in a coaxial tube as solvent for lock.

IR Spectra.—The IR spectra were recorded in the solid state on a Bruker IFS 113 V Fourier Transform Spectrophotometer using KBr pellets in the 4000–400 cm^{-1} region. For liquid-film investigations, a Perkin-Elmer Spectrophotometer, equipped with NaCl pellets, was used in the 4000–200 cm^{-1} region.

TGA.—The thermogravimetric analysis was performed with a Mettler TA3000 Analyser (Start temperature: 35 °C; end temperature: 300 °C; scan rate: 10 K min^{-1}).

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