

*In memoriam prof. dr. Ioan A. Silberg*

## SPECTRAL INVESTIGATION OF 3-MERCAPTO-1,2,4-TRIAZOLE LIGANDS

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**ABSTRACT.** Preliminary spectral studies on 5-aryl-3-mercapto-1,2,4-triazoles,  $\text{Ar-C}_2\text{H}_2\text{N}_3\text{S}$ ,  $\text{Ar} = \text{C}_6\text{H}_5$ - (1), 4- $\text{H}_3\text{CC}_6\text{H}_4$ - (2), 4- $\text{ClC}_6\text{H}_4$ - (3) and 4- $\text{BrC}_6\text{H}_4$ - (4) and 5,5'-(1,4-phenylene)-bis(3-mercapto-1,2,4-triazole), 1,4- $\text{C}_6\text{H}_4(\text{C}_2\text{H}_2\text{N}_3\text{S})_2$  (5) are discussed. The FT-IR and  $^1\text{H}$  NMR spectra of 1-5 are consistent with the structure of triazole rings and aromatic systems. The IR data recorded for 1-5 and Raman data recorded for 5 confirm the occurrence of the thiol tautomeric form of the heterocycle in solid state. The  $^1\text{H}$  NMR data are consistent with the presence of the thioamido (thione) form in solution. All spectra suggest a mixture of thione/thiol tautomers in both solid state and solution.

**Keywords:** mercaptotriazole, FT-IR, FT-Raman,  $^1\text{H}$  NMR.

## INTRODUCTION

The N and N-S heterocyclic derivatives (i.e. mercapto-thiadiazoles, mercapto-triazoles and –tetrazoles, etc.) remain of great interest in coordination and supramolecular chemistry. The flat, rigid geometry of such heterocycles, along with their increased number of heteroatoms, encourage the association of these molecules into outstanding supramolecular structures. The self-assembly pattern and the resulting architectures depend – among other criteria – on the extension and nature of interacting atoms/groups. More specific, crystallographic evidences proved in several cases that heterocycles containing thioamido groups ( $\text{HN-C=S}$ ) generate multiple  $\text{N-H}\cdots\text{E}$  ( $\text{E} = \text{N}, \text{O}, \text{S}$ ) hydrogen bonding [1-5]. For example, the co-crystallization of 1,3,5-triazine-2,4,6-trithione,  $\text{C}_3\text{N}_3\text{S}_3\text{H}_3$  (also known as trimercaptotriazine or trithiocyanuric acid) with melamine, tricyanuric acid, 4,4'-bipyridine, etc. produced supramolecular structures with nanometric cavities and channels.

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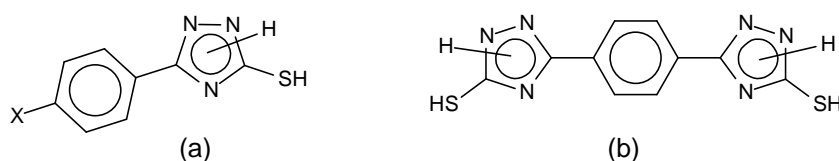
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Many of these compounds have proved excellent zeolitic properties [1-3]. On the other hand, the thione sulfur atoms may involve in intermolecular S...S interactions, which have been found of great importance in the supramolecular construction of molecular electronics [6]. It is the case of dimercapto-thiadiazole,  $C_2H_2N_2S_3$  and phenyl-dimercapto-thiadiazole,  $C_6H_5-C_2HN_2S_3$  (also known as Bismuthiol I and II, respectively) that revealed short S...S interactions (3.4 – 3.7 Å) in metal complexes [7].

Deprotonation of such heterocycles usually leads to anions in their thiolato tautomeric form. Coordination of the anionic ligand to metal centers through sulfur may generate a large variety of molecular structures, ranging from mono- and dinuclear units [i.e. trithiocyanuric complexes of Na and Cu(I) [4]; organotin(IV) complexes of Bismuthiol II [7], etc.] to infinite 1D or 2D polymers [i.e. organotin(IV) complexes of Bismuthiol II [7], Au(I) complexes of Bismuthiol I, [8,9] etc.].

We have recently initiated the vibrational and crystallographic investigation of a new range of  $\pi$ -excessive heterocyclic systems derived from Bismuthiol I [10-13]. Due to the encouraging results concerning the involvement of the heterocycles in self-assembly and the increased role of heteroatoms in such interactions, we decided to vary the number of nitrogen vs. sulfur atoms. In this respect, we decided to focus on 5-aryl-3-mercapto-1,2,4-triazoles as potential candidates for coordination and supramolecular chemistry, due to the lack of crystallographic evidences for such species [14].

Hence, the aim of this work is the preliminary spectral characterization of 5-aryl-3-mercapto-1,2,4-triazoles, 4- $XC_6H_4-C_2H_2N_3S$ , X = H (**1**),  $CH_3$  (**2**), Cl (**3**) and Br (**4**) (Scheme I.a) and 5,5'-(1,4-phenylene)-bis(3-mercapto-1,2,4-triazole), 1,4- $C_6H_4(C_2H_2N_3S)_2$  (**5**) (Scheme I.b). Despite the possibility of several thione (thioamide) and thiol tautomers, the Scheme I illustrates only the thiol form for simplicity.



Scheme I

## RESULTS AND DISCUSSION

Five mercaptotriazole derivatives **1** – **5** have been prepared and characterized by vibrational and  $^1H$  NMR.

The FT-IR spectra of **1** – **5** were recorded in the 4000 – 400  $cm^{-1}$  spectral range. For the bis-mercaptotriazole (**5**), the Raman spectrum was recorded in the 3500 – 200  $cm^{-1}$  spectral range. The most relevant spectral data are listed in Table 1 and 2.

Table 1

Selected FT-IR data ( $\text{cm}^{-1}$ ) for compounds **1** – **4**.

$\text{C}_2\text{H}_3\text{N}_3\text{S}$ [17]	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	Assignment
		3433 mw	3446 w	3446 mw	$\nu(\text{OH})$
3150 <i>w</i> *	3089 sh	3130 sh	3105 sh	3100 sh	$\nu(\text{NH})$
3080 <i>w</i>	3060 <i>s</i>	3086 <i>s</i>	3057 <i>s</i>	3055 <i>s</i>	$\nu(\text{CH})$
	3003 <i>s</i>	3020 <i>s</i>	3035 <i>s</i>	2989 <i>s</i>	
	2642 <i>m</i>	2692 mw	2665 <i>m</i>	2663 mw	$\nu(\text{SH})$
2565 <i>w</i>	2577 <i>m</i>	2594 <i>w</i>	2580 mw	2582 <i>w</i>	
	1593 mw	1618 <i>m</i>	1608 <i>s</i>	1604 <i>s</i>	Ar quadrant stretching
	1582 <i>w</i>	1593 <i>s</i>	1588 <i>m</i>	1581 <i>m</i>	
1559 <i>s</i>	1566 <i>s</i>	1565 <i>s</i>	1562 <i>s</i>	1560 <i>s</i>	$\nu(\text{CN})$
1460 <i>vs</i>	1508 <i>vs</i>	1525 <i>vs</i>	1506 <i>vs</i>	1504 <i>vs</i>	$\nu(\text{CN})$
	1485 <i>s</i>	1485 <i>s</i>	1484 <i>s</i>	1481 <i>ms</i>	Ar semicircle stretching +
	1453 <i>m</i>	1460 <i>s</i>	1439 <i>m</i>	1439 <i>m</i>	$\delta(\text{CH})$ ip
1430 <i>vw</i>	1423 mw		1426 <i>m</i>		$\nu(\text{CN})$
	1290 <i>w</i>	1288 <i>w</i>	1294 <i>w</i>	1294 <i>w</i>	$\delta(\text{CH})$ ip
1260 <i>s</i>	1225 <i>ms</i>	1234 <i>s</i>	1228 <i>m</i>	1228 <i>m</i>	$\nu(\text{NN})$
1187 <i>vs</i>					$\delta(\text{NH})$
		1119 mw	1110 <i>w</i>	1106 <i>w</i>	$\delta(\text{CH})$ ip
			1095 <i>s</i>		$\nu(\text{CCI})$
944 <i>vs</i>	966 <i>ms</i>	976 <i>m</i>	968 <i>ms</i>	966 <i>m</i>	$\nu(\text{CS})$
	918 <i>w</i>	818 <i>m</i>	835 <i>s</i>	833 <i>s</i>	$\delta(\text{CH})$ op
	785 <i>ms</i>		786 <i>w</i>	783 <i>w</i>	
	699 <i>s</i>	715 <i>m</i>	727 <i>m</i>	725 <i>ms</i>	Ar op bending by sextants
701 <i>ms</i>	686 <i>s</i>	691 mw	690 <i>w</i>	688 <i>w</i>	$\delta(\text{CSH})$ ip
526 <i>w</i>	540 <i>m</i>	538 <i>m</i>	552 <i>w</i>	557 mw	$\delta(\text{NCS})$ ip
485 <i>vw</i>	469 <i>vw</i>	474 <i>w</i>	462 <i>w</i>	479 <i>vw</i>	$\delta(\text{CSH})$ op

Abbreviations: *w* – weak, *mw* – medium weak, *m* – medium, *ms* – medium strong, *s* – strong, *vs* – very strong, *br* – broad, *sh* – shoulder,  $\nu$  - stretching,  $\delta$  - bending, *ip* – in plane, *op* – out of plane, Ar – aromatic ring.

\* IR data from reference 18.

The following discussion is based on the comparison between our spectral data recorded for **1** – **5** and the known literature data published for the unsubstituted 3-mercapto-1,2,4-triazole,  $\text{C}_2\text{H}_3\text{N}_3\text{S}$  [17,18].

The 4000 – 2000  $\text{cm}^{-1}$  spectral range is relevant for the characterization of NH, CH and SH groups. The characteristic stretching modes give rise to a large and complex band in the IR spectra of all compounds. The best

described peaks are assigned to  $\nu(\text{CH})$  at  $3086 - 3055 \text{ cm}^{-1}$ , while the  $\nu(\text{NH})$  mode can be hardly distinguished as a shoulder at  $3130 - 3089 \text{ cm}^{-1}$ . However, the assignment of  $\nu(\text{NH})$  at  $3150 \text{ (IR)}$  [18] and  $3156 \text{ cm}^{-1}$  (Raman) [17] for 3-mercapto-1,2,4-triazole support our interpretation.

**Table 2**

Selected FT-IR and Raman data ( $\text{cm}^{-1}$ ) for compound **5**.

IR	Raman	Vibrational Assign.
3433 mw		$\nu(\text{OH})$
3103 m	3109 vw, sh	$\nu(\text{NH})$
3068 m	3063 vw	$\nu(\text{CH})$
2997 m	2997 vw	
2683 w		$\nu(\text{SH})$
2596 w	2577 vw	
1595 s	1592 w	Ar quadrant stretching
1527 s	1554 w	$\nu(\text{CN})$
1493 s	1496 s	$\nu(\text{CN})$
1458 m	1473 m	Ar semicircle stretching + $\delta(\text{CH})$ ip
1436 m	1433 w	$\nu(\text{CN})$
1294 w	1300 w	$\delta(\text{CH})$ ip
1236 s	1245 w	$\nu(\text{NN})$
1105 m	1106 vw	$\delta(\text{CH})$ ip
964 ms	967 w	$\nu(\text{CS})$
858 w	863 vw	$\delta(\text{CH})$ op
766 w	749 vw	
706 m		Ar op bending by sextants
667 m	668 vw	$\delta(\text{CSH})$ ip
528 m		$\delta(\text{NCS})$ ip
471 w		$\delta(\text{CSH})$ op

Vibrational investigations on various mercaptans have located the SH stretching in the approx.  $2650 - 2500 \text{ cm}^{-1}$  range, as a well defined, medium to weak band [15, 17, 19]. The IR spectra of **1** – **5** reveal distinctive peaks in the mentioned range, which may be assigned to the  $\nu_{\text{as}}(\text{SH})$  ( $2692 - 2642 \text{ cm}^{-1}$ ) and  $\nu_{\text{s}}(\text{SH})$  ( $2596 - 2577 \text{ cm}^{-1}$ ) modes. In addition, the Raman spectrum of **5** shows a weak but very neat band at  $2577 \text{ cm}^{-1}$ , which definitely support the previous assignment.

The 2000 – 1000  $\text{cm}^{-1}$  spectral range is relevant mainly for the characterization of the heterocyclic skeleton. The most important bands fall in the 1560 – 1527, 1525 – 1493 and 1436 – 1423  $\text{cm}^{-1}$  regions for  $\nu(\text{CN})$ , and 1234 – 1225  $\text{cm}^{-1}$  range for  $\nu(\text{NN})$ . In addition, at least one assignment should be made for the  $\delta(\text{NH})$  or  $\delta(\text{CNH})$  modes at approx. 1470 – 1420 and/or 1200  $\text{cm}^{-1}$  [17, 19]. However, this assignment proved very difficult due to the overlap with other bands.

The 1000 – 400  $\text{cm}^{-1}$  spectral range brings new evidences for the identity of the CS group. Thus, the assignment of the band located in the 976 – 964  $\text{cm}^{-1}$  region to the  $\nu(\text{CS})$  fundamental is in good agreement with the spectral data published for 3-mercapto-1,2,4-triazole in its thiol tautomeric form (944  $\text{cm}^{-1}$ ) [17-18]. Moreover, this value is significantly lower than that found for thione CS groups in related heterocycles [i.e. thiadiazole-thiones,  $\nu(\text{CS})$  approx. 1060 – 1040  $\text{cm}^{-1}$ ] [10-13]. The presence of the thiol tautomer in solid state is also suggested by the location of the  $\delta(\text{CSH})$  bands at 691 – 667 and 479 – 462  $\text{cm}^{-1}$ .

The  $^1\text{H}$  NMR spectra of compounds **1** – **4** were recorded in ordinary DMSO- $\text{d}_6$  at room temperature and are largely unexceptional as it concerns the characterization of aryl groups (Tab. 3). The spectrum of **5** was of unsatisfactory quality due to its poor solubility. According to literature data, the thioamido (NH) and thiol (SH) protons should fall into the 8-11/13-14 ppm and 2-6 ppm range, respectively [20-22]. The four spectra show small but clear broad singlets at 13.66-13.78 ppm, which may be assigned to thioamido protons. In addition, the spectra reveal singlets located at 3.48-3.61 ppm for each compound. These peaks can be only tentatively assigned to SH protons as long as humidity is present in compounds and/or deuterated solvent.

Table 3

$^1\text{H}$  NMR data ( $\delta$  in ppm, J in Hz) for compounds **1** - **5**.

<b>1</b>	$\delta$ 13.71 (s br, 1H, NH), 7.87 (m, 2H, 2- $\text{C}_6\text{H}_5$ ), 7.45 (m, 3H, 3,4- $\text{C}_6\text{H}_5$ ), 3.61 (bs, $\text{H}_2\text{O}/\text{SH}$ ).
<b>2</b>	$\delta$ 13.66 (s br, 1H, NH), 7.78 (d, 2H, 2- $\text{C}_6\text{H}_4$ , $^3\text{J}$ 8.1), 7.32 (d, 2H, 3- $\text{C}_6\text{H}_4$ , $^3\text{J}$ 8.4), 3.48 (s, $\text{H}_2\text{O}/\text{SH}$ ), 2.35 (s, 3H, $\text{CH}_3$ ).
<b>3</b>	$\delta$ 13.77 (s br, 1H, NH), 7.90 (d, 2H, 2- $\text{C}_6\text{H}_4$ , $^3\text{J}$ 8.7), 7.58 (d, 2H, 3- $\text{C}_6\text{H}_4$ , $^3\text{J}$ 8.5), 3.51 (bs, $\text{H}_2\text{O}/\text{SH}$ ).
<b>4</b>	$\delta$ 13.78 (s br, 1H, NH), 7.83 (d, 2H, 2- $\text{C}_6\text{H}_4$ , $^3\text{J}$ 8.7), 7.73 (d, 2H, 3- $\text{C}_6\text{H}_4$ , $^3\text{J}$ 8.5), 3.48 (bs, $\text{H}_2\text{O}/\text{SH}$ ).

## CONCLUSIONS

The preliminary spectral investigation of **1** – **5** brings evidences for the identity of heterocyclic and aryl fragments. The FT-IR and Raman spectra strongly suggest the presence of the thiol tautomers in solid state and suspect, with rather poor arguments, the presence of the thione (thioamide) forms. Alternatively, the  $^1\text{H}$  NMR spectra of **1** – **4** suggest the presence of the thioamide forms in solution and only suspect the thiol tautomers. Further Raman measurements, as well as complete  $^1\text{H}$  and  $^{13}\text{C}$  NMR investigations in dry deuterated solvent will be performed in order to elucidate the present ambiguities.

## EXPERIMENTAL PART

FT-Raman spectra on solid samples were recorded using a Bruker FT-IR Equinox 55 Spectrometer equipped with an integrated FRA 106 S Raman module. The excitation of the Raman spectra was performed using the 1064 nm line from a Nd:YAG laser with an output power of 250 mW. An InGaAs detector operating at room temperature was used. FT-IR spectra were recorded on KBr pellets, using a FT-IR JASCO 600 Spectrometer. The spectral resolutions were  $2\text{ cm}^{-1}$ . Room-temperature  $^1\text{H}$  NMR spectra were recorded in ordinary  $\text{DMSO-d}_6$  on a BRUKER AVANCE 300 instrument operating at 300.11 MHz. The chemical shifts are reported in ppm relative to the residual peak of the deuterated solvent (ref. DMSO:  $^1\text{H}$  2.49 ppm).

The starting materials were purchased from commercial sources as analytical pure reagents and were used with no further purification. Compounds **1** – **5** were prepared following a literature protocol [15,16]. The thiosemicarbazide was reacted with acyl chloride in 2N NaOH solution and the resulting acyl-thiosemicarbazide was isolated in HCl medium, filtered and recrystallized from ethanol. The intermediate was re-dissolved in 2N NaOH solution and refluxed for approx. 1.5 hours. After filtering and diluting the reaction mixture, the mercapto-triazoles were precipitated with aqueous HCl, filtered and recrystallized from ethanol (**1**, **3**, **4**), water (**2**) or ethanol/dmfa (**5**). In all cases, the products were isolated as white microcrystalline solids. MP ( $^{\circ}\text{C}$ ): 262-4 (**1**), 267-8 (**2**), 296-8 (**3**), 294-5 (**4**) and  $>300$  (**5**).

## ACKNOWLEDGEMENTS

M.M.V. thanks The National University Research Council Romania for financial support during the course of this work (grant CNCSIS-A 14/1449/2007). The authors also thank Dr. Simona Cinta Pinzaru (Babes-Bolyai University, Dept. of Physics) for facilitating Raman measurements.

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