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Dedicated to Professor Ionel Haiduc,
President of The Romanian Academy at his 70th anniversary

NEW GROUP 2 METAL SALTS OF MONODEPROTONATED (3*H*-2-THIOXO-1,3,4-THIADIAZOL-2-YL)THIOACETIC ACID. SYNTHESIS AND VIBRATIONAL CHARACTERIZATION

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ABSTRACT. Reaction of the monosodiul salt of (3*H*-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetic acid with group 2 metal halides produced the corresponding Mg, Ca, Sr and Ba derivatives. Preliminary vibrational studies on this new series are discussed in terms of FT-IR and FT-Raman spectroscopy. The spectral data are consistent with the deprotonation of the carboxylic unit and the thione tautomeric form of the heterocycle.

Key-words: (3*H*-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetic acid, group 2 metals, FT-IR and Raman spectroscopy.

Introduction

We have recently initiated structural investigations on the new (3*H*-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetic acid and a large range of d metal complexes containing the ligand in its monodeprotonated form.[1-3] These studies follow our on-going interest in the chemistry of mercapto-aza type heterocyclic derivatives (i.e. trithiocyanuric acid, *Bismuthiol I* and *II)*, which have been proved valuable candidates for coordination and supramolecular chemistry.[4-6] In addition, such compounds have found extensive application in analytical chemistry as well as industry.[7-10]

In this paper we wish to report further on the chemistry of 3*H*-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetic acid, $C_2HN_2S_3CH_2COOH$ (**1**). Compound **1**, which can theoretically exist in either thiol (N=C-SH) or thione (HN-C=S) forms (Scheme I), derives from the well known dimercapto-thiadiazol, $C_2H_2N_2S_3$ (also known as *Bismuthiol I*) by substitution at one of the two SH groups.[1] There are two main reasons for such a substitution. First, the insertion of a new functional group (i.e. carboxyl) might enhance the coordination behavior of the ligand. Second, the asymmetric substitution allows the

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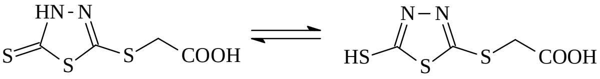
conservation of a protonated NCS unit which proved valuable in generating interesting intermolecular interactions, such as coordination (i.e. S-monodentate and S,N-bidentate chelating), hydrogen bonding (i.e. N-H···E, E = N, O, S) and S···S interactions.[5-6]



Scheme I

Recent crystallographic investigation on the mono-sodium salt of **1**, $[Na(C_2HN_2S_3CH_2COO)(H_2O)_4]\cdot H_2O$ (**2**) showed that the molecular structure does not resume to a simple salt but reveals both coordination of the monodeprotonated ligand to Na^+ (i.e. $C=S\rightarrow Na$) and intermolecular hydrogen bonding and S···S interactions.[3] In this respect, we have decided to extend our studies in the range of group 2 metal homologues: $[M(C_2HN_2S_3CH_2COO)_2]$, M = Mg, **3**; Ca, **4**; Sr, **5**; Ba, **6**. Therefore, the aim of this work is the synthesis of the title series of new derivatives (**3** – **6**) along with their FT-IR and Raman characterization. The vibrational studies could elucidate the occurrence of the thione *vs.* thiol tautomeric form of the heterocyclic unit in solid state and suggest the most probable coordination sites of the ligand.

Experimental

FT-IR and 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. The spectral resolution was 2 cm^{-1}.

The starting materials were purchased from commercial sources as analytical pure reagents and were used with no further purification. The (3*H*-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetic acid (**1**) and its monosodium salt (**2**) were prepared following a literature protocol.[1,2]

The group 2 metal derivatives of **1** as monodeprotonated forms **3** – **6**, $[M(C_2HN_2S_3\text{-}CH_2COO)_2]$, M = Mg, **3**; Ca, **4**; Sr, **5**; Ba, **6**, were synthetised by reacting stoechiometric amounts of **2** with corresponding metal halides $MgCl_2\cdot 6H_2O$, $CaCl_2$, $SrCl_2\cdot 6H_2O$ and $BaCl_2\cdot 2H_2O$, respectively, in aqueous solution, at room temperature. Preliminary microanalysis of **2** proved that the monosodium salt is tetrahydrated in solid state. However, the stoechiometry was related to anhydrous products. Therefore, the yields will be corrected as soon as microanalysis will establish the degree of hydratation of **3** – **6**. In all cases, the products precipitated at once. After stirring the reaction mixtures for about 30 minutes, the crude products were filtered and recrystallized from warm distilled water, as colorless crystalline solids. Preparation details and brief characterization of compounds **3** – **6** are given in Table 1.

Table 1.

Preparation details and characterization of compounds **3** – **6.**

No.	Compound*	Yield* (%)	mp (°C)
3	$[Mg(C_2HN_2S_3\text{-}CH_2COO)_2]$	52	224-226
4	$[Ca(C_2HN_2S_3\text{-}CH_2COO)_2]$	57	185-187
5	$[Sr(C_2HN_2S_3\text{-}CH_2COO)_2]$	58	226-228 (dec)
6	$[Ba(C_2HN_2S_3\text{-}CH_2COO)_2]$	52	268-270 (dec)

* Due to the lack of microanalysis, the lattice water was ignored in calculations.

Results and discussion

Partial neutralisation of (3*H*-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetic acid, $C_2HN_2S_3\text{-}CH_2COOH$ (**1**) with sodium bicarbonate produced the monosodium salt, $[Na(C_2HN_2S_3\text{-}CH_2COO)]$ (**2**).[1,2] Compound **2** was further used in the preparation of four new alkali-earth metal homologues, $[M(C_2HN_2S_3CH_2COO)_2]$, M = Mg, **3**; Ca, **4**; Sr, **5**; Ba, **6** (eq. 1). All the reactions worked in aqueous media, at room temperature. Compounds **3** – **4** are soluble in hot water and were isolated as crystalline solids. All metal derivatives are air and light stable in both solution and solid state.

$$2\,[Na(C_2HN_2S_3\text{-}CH_2COO)] + MCl_2 \rightarrow [M(C_2HN_2S_3CH_2COO)_2] + 2\,NaCl \quad \text{(eq. 1)}$$

The FT-IR and Raman spectra of **3** – **6** were recorded in the 4000 – 400 and 3500 – 200 cm^{-1} spectral ranges, respectively. For the magnesium compound **3**, the Raman spectrum could not be recorded. The most relevant spectral data are listed in Table 2. The following discussion is based on the comparison between the current spectral data recorded for **3** – **6** and the known literature data for **1** and **2**.[1,2]

The 4000 – 2000 cm^{-1} spectral range is relevant for the characterization of EH groups (E = O, N, C and S) in IR and/or Raman spectra. The complex carboxylic OH band present in the IR spectrum of **1** (approx. 3100 - 2800 cm^{-1}) disappears in the IR spectra of **3** - **6**, similarly to **2**, as a result of deprotonation of the carboxylic group. The IR spectra show also broad bands at 3446 - 3334 cm^{-1}, which are assigned to the $\nu(H_2O)$ modes. The $\nu(NH)$ fundamental becomes difficult to locate due to the overlap with the broad $\nu(H_2O)$ band previously mentioned. The lack of the characteristic $\nu(SH)$ bands – usually assigned at 2600 – 2400 cm^{-1} – in both IR and Raman spectra of **3** - **6**, confirms the occurrence of the thione tautomer in solid state. In addition, al spectra are consistent with the presence of aliphatic CH groups.

Table 2.

Selected vibrational data (cm^{-1}) for compounds **2** – **6**.

2*		3**	4		5		6		Vibrational assignment
IR	Ra	IR	IR	Ra	IR	Ra	IR	Ra	
3487 – 3388 m,br		3406 s,br	3446 s,br		3421 – 3334 s,br		3446 s,br		$\nu(H_2O)$
3106 sh	2976 w				3088 sh		3109 w,sh		$\nu(NH)$
2939 w	2940 m	2921 w	2922 m	2927 s	2922 w	2924 m	2921 w	2922 m	$\nu_{as}(CH)$
2893 w		2845 w	2852 m		2873 w		2852 w		$\nu_s(CH)$
		1630 vs					1651 mw		$\delta(H_2O)$
1604 vs	1611 vw	1577 vs	1601 vs	1596 vw	1603 vs	1610 vw	1581 vs	1629 vw	$\nu_{as}(COO)$
1518 ms	1515 vw	1527 s	1533 s	1531 vw	1541 ms	1540 vw	1539 s 1456 mw	1533 vw	$\nu(NC)+\delta(NH)$
1454 m	1457 vs	1450 m	1448 m	1448 vs	1446 m	1446 vs		1454 vs	
1410 s	1406 w	1396 s	1396 s	1396 w	1383 s	1384 m	1394 s	1393 m	$\delta(CH_2)$
1117 m	1110 w	1106 w	1101 mw	1104 w	1101 mw	1103 mw	1119 w	1108 w	$\nu(NN)$
1053 s	1055 m	1051 s	1053 s	1060 m	1055 s	1060 m	1053 s	1063 m	$\nu_{as}(S\text{-}C{=}S)$
717 m	723 w	717 s	717 s		717 ms		719 m	726 vw	$\nu_{as}(CSC)_{endo}$
650 w	655 s	646 m	666 m	662 s	650 m	660 s	650 w	656 s	$\nu_s(CSC)_{endo}$

Abbreviations: Ra – Raman, w – weak, mw – medium weak, m – medium, ms – medium strong, s – strong, vs – very strong, br – broad, sh – shoulder, ν - stretching, δ - bending, endo – endocyclic.

* Literature data.[2]

** The Raman spectrum of **3** could not be recorded.

The 2000 – 1000 cm^{-1} spectral range is relevant for both heterocyclic and alkyl-carboxylic units of the monodeprotonated acid. The most important vibrational modes which characterize the heterocyclic unit are the ν(C=N), ν(N-N) and ν_{as}(S-C=S) stretchings, assigned in the spectra of **3** - **6** at 1541-1527 and 1456-1446, 1119-1101 and 1063-1051 cm^{-1}, respectively. All spectral data previously mentioned are in good agreement with the corresponding fundamentals reported for compound 1 or homologue heterocyclic derivatives.[1,11]

In addition to the lack of carboxylic ν(OH) in the approx. 3100 - 2800 cm^{-1} spectral range, the current region brings new information in support of carboxyl group deprotonation. Thus, the ν(C=O) mode assigned for **1** at 1693 cm^{-1} shifts to significantly lower wavenumbers in the spectra of **3** – **6** as a consequence of electron delocalization [ν_{as}(COO) 1629 – 1577 cm^{-1}]. As it concerns the ν_{s}(COO) fundamentals, it proved again difficult to choose between the plethora of bands located in the expected region (approx. 1450 – 1300 cm^{-1}).[12] In our previous works we have tentatively assigned this mode at 1333 – 1290 cm^{-1}, probably overlapping ν(CN) modes.[2,3] Despite the existence of homologues bands in all spectra of **3** – **6** (1309 – 1302 cm^{-1}), we shall not insist on this assignment until new spectroscopic results will support our supposition.

The 1000 – 200 cm^{-1} spectral range shows no unusual features. Many bands located in this region are assigned to group bending and other skeleton fundamentals (i.e. ν_{as}(CSC)$_{endo}$ 726 – 717 and ν_{s}(CSC)$_{endo}$ 666 – 646 cm^{-1}).

Conclusions

Both heterocyclic unit and side chain of the monodeprotonated ligand are well represented in the IR and Raman spectra. It can be concluded that the deprotonation of **1** takes place at the COOH group, while the remaining proton is located on the endocyclic nitrogen atom, giving rise to the thione tautomer. While the ν_{as}(COO) mode is undoubtedly assigned in the 1603 – 1577 cm^{-1} range, its ν_{s}(COO) counterpart is hard to locate.

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