

Dedicated to Professor Ionel Haiduc
on the occasion of his 70th anniversary

NEW METAL COMPLEXES OF MONOANIONIC (3*H*-2-TIOXO-1,3,4-THIADIAZOL-5-IL)-THIOACETIC ACID. X-RAY STRUCTURE OF [Na(C₂N₂HS₃CH₂COO)(H₂O)₄]₂·2H₂O

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Partial neutralization of (3*H*-2-tioxo-1,3,4-thiadiazol-5-yl)thioacetic acid, C₂HN₂S₃CH₂COOH (**1**) with one equivalent of s metal carbonates (Na, K) produced the corresponding salts: M(C₂HN₂S₃CH₂COO), M = Na (**2**) and K (**3**), which were further used in the preparation of a new Mn(II) complex (**4**) containing the mono-anionic ligand. The FT-IR and FT-Raman studies performed on the title compounds reveal the deprotonation of the carboxylic group and the presence of the thione tautomeric form of the heterocyclic unit in solid state. The molecular structure of **2** as hydrate, [Na(C₂HN₂S₃CH₂COO)(H₂O)₄]₂·2H₂O was determined by single-crystal X-ray diffraction. The sodium atoms of the dinuclear unit display octahedral SNaO₅ coordination spheres linked through water bridges. The ligand binds to sodium through the thione sulfur, revealing a monodentate coordination behavior.

INTRODUCTION

We have recently initiated the structural investigation of new mercapto-aza type heterocyclic derivatives, including both organic compounds and corresponding metal complexes.¹⁻⁵ Related molecular systems, such as dimercaptothiadiazole, C₂H₂N₂S₃ (also known as Bismuthiol I) or 1,3,5-triazine-2,4,6-trithione, C₃N₃S₃H₃ (also known as trimercaptotriazine or trithiocyanuric acid) proved excellent candidates for coordination and supramolecular chemistry in general, and crystal engineering in particular, due to their main structural attributes: flat, rigid molecular geometry and increased number of heteroatoms E and EH groups (E: O, N, S, etc.).⁶⁻¹²

In this respect, we have focused on the preparation of new organic derivatives by increasing and diversifying the number of heteroatoms E and EH groups on π-excessive heterocyclic systems. Thus, the extension of

Bismuthiol I skeleton (Fig. 1a) with alkyl-carboxylic fragments, through one exocyclic sulfur, produced a range of three 3*H*-5-carboxyalkylthio-2-tioxo-1,3,4-thiadiazole derivatives, C₂HN₂S₃(CH₂)_nCOOH (n = 1 – 3) (Fig. 1b) which were investigated using FT-IR and FT-Raman spectroscopy.⁴

Further, compound **1** was partially deprotonated to form the corresponding monosodium salt, Na(C₂HN₂S₃CH₂COO) (**2**) which was used as precursor in the preparation of four new d metal complexes, M(C₂HN₂S₃CH₂COO)₂ (M = Co, Ni, Cu, Zn). All of these compounds have been characterized by advanced vibrational methods.⁵

Once we have managed to determine the molecular structure of **2** as hydrate, [Na(C₂N₂HS₃CH₂COO)(H₂O)₄]₂·2H₂O (which will be discussed later in this work) and noticed the outstanding structural features, our interest for such s metal derivatives increased beyond the limits of simple precursors. Hence, the aim of this

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work is the synthesis of new s and d metal complexes of **1** in its monoanionic form along with their structural characterization in terms of FT-IR

and Raman spectroscopy as well as single-crystal X-ray diffraction.

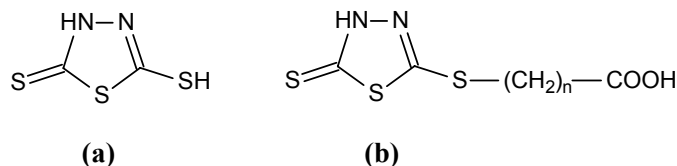


Fig. 1 – Schematic drawing of Bismuthiol I (a) and 3*H*-5-carboxyalkylthio-2-tioxo-1,3,4-thiadiazole derivatives ($n = 1 - 3$) (b).

RESULTS

One new potassium derivative and one new manganese(II) complex of mono-deprotonated (3*H*-2-tioxo-1,3,4-thiadiazol-5-yl)thioacetic acid (**1**), $\text{K}(\text{C}_2\text{HN}_2\text{S}_3\text{CH}_2\text{COO})$ (**3**) and $[\text{Mn}(\text{C}_2\text{HN}_2\text{S}_3\text{CH}_2\text{COO})_2]$ (**4**), have been prepared following the synthetic procedures proposed for the corresponding monosodium salt, $\text{Na}(\text{C}_2\text{HN}_2\text{S}_3\text{CH}_2\text{COO})$ (**2**) and d metal homologues, respectively reported previously.⁵ The direct reaction of **1** with one equivalent of potassium bicarbonate produced compound **3** as colorless crystalline solid. Further, reaction of the monosodium (**2**) or mono-potassium (**3**) salts with the equivalent amount of manganese sulfate produced compound **4** also as colorless crystalline solid. All reactions worked in good yields (63 – 92%). All new derivatives are soluble in water. In solid state, in open atmosphere and at room temperature, they

slowly loose lattice water. Single-crystals as colorless plates were grown for **2** from hot aqueous solution and subjected to single-crystal X-ray diffraction analysis.

The molecular structure of **2** as hydrate, $[\text{Na}(\text{C}_2\text{N}_2\text{HS}_3\text{CH}_2\text{COO})(\text{H}_2\text{O})_4]_2 \cdot 2\text{H}_2\text{O}$ is presented in Fig. 2 along with the atom numbering scheme. This structure is the first crystallographic proof of a (5-(3*H*-2-tioxo-1,3,4-thiadiazol-5-yl)thioacetato derivative. All the ligands and lattice water molecules are involved in extensive intermolecular hydrogen bonding. The pattern of these interactions as well as the detailed description of the crystal structure will be given elsewhere.

The FT-IR and FT-Raman spectra of compounds **3** and **4** were recorded in the 4000 – 400 and 3500 – 200 cm^{-1} spectral range, respectively. The most relevant spectral data are listed in Table 1 along with the corresponding values obtained for compound **2**.⁵

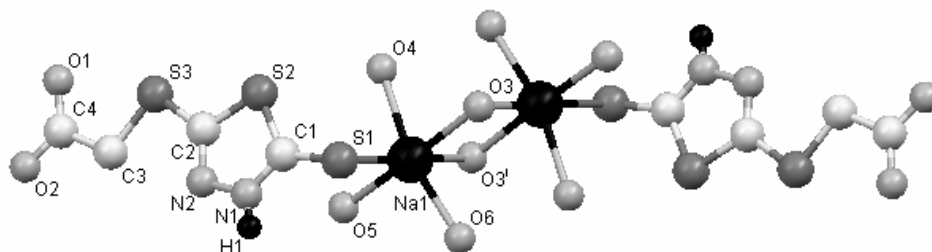


Fig. 2 – The molecular structure of **2** showing the labeling scheme used in discussion. The alkyl and water hydrogen atoms as well as the two lattice water molecules were omitted for clarity.

Table 1

Selected vibrational data (cm^{-1}) for compounds **2** – **4**

2*		3		4		Vibrational assignment
IR	Ra	IR	Ra	IR	Ra	
3487 m		3448 s		3416 s		$\nu(\text{H}_2\text{O})$
3388 m		3394 ms		3375 s		
3106 w,sh		3116 m		3093 m		$\nu(\text{NH})$

Table 1 (continues)

Table 1 (continued)

2939 w	2976 m	2968 w	2969 w	2970 m	2972 w	$\nu_{\text{as}}(\text{CH})$
2893 w	2940 s	2910 m	2930 m	2917 m	2932 m	$\nu_{\text{s}}(\text{CH})$
1604 vs	1611 vw	1603 vs	1618 vw	1587 vs	-	$\nu_{\text{as}}(\text{COO})$
1518 ms	1515 vw	1541 s	-	1537 s	1533 vw	$\nu(\text{NC})+\delta(\text{NH})$
1454 m	1457 vs	1452 m	1451 vs	1444 m	1443 vs	
1410 s	1406 w	1408 m	-	1402 s	1399 w	$\delta(\text{CH}_2)$
1298 vs	1290 m	1306 vs	1301 m	1306 vs	1310 s	$\nu_{\text{s}}(\text{COO}) / \nu(\text{NC})$
1117 m	1110 w	1117 m	1101 w	1117 m	1113 m	$\nu(\text{NN})$
1053 s	1055 m	1051 vs	1056 m	1051 vs	1059 ms	$\nu_{\text{as}}(\text{S-C=S})$
717 m	723 w	719 m	723 w	719 m	729 vw	$\nu_{\text{as}}(\text{CSC})_{\text{endo}}$
650 w	655 s	648 w	654 s	648 w	662 s	$\nu_{\text{s}}(\text{CSC})_{\text{endo}}$

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, as – asymmetric, s – symmetric.

* Literature data.⁵

DISCUSSION

The discussion of the FT-IR and FT-Raman spectra of the new compounds is based on the comparison between the experimental data recorded for **3** and **4** and the literature data published for **2**.⁵ The NH, OH, SH and CH groups are best described in the 4000 – 2000 cm^{-1} spectral range. Thus, the deprotonation of the carboxylic group is suggested by the disappearance of the large and complex band (approx. 3100 – 2700 cm^{-1}) present in the IR spectrum of the acid (**1**)^{4,5} as well as the preservation of the $\nu(\text{NH})$ mode (3116 – 3093 cm^{-1}) in the same spectra of **2** – **4**. The aliphatic CH groups are well represented by the characteristic bands (ν_{as} and ν_{s}) assigned in the 2976 – 2893 cm^{-1} region, in both IR and Raman spectra. Moreover, the large IR bands centered at 3487 – 3416 and 3394 – 3375 cm^{-1} are consistent with the $\nu(\text{H}_2\text{O})$ fundamentals and reveal the presence of water in all compounds. As it concerns the SH group, all spectra lack the characteristic $\nu(\text{SH})$ bands, which should be assigned in the approx. 2600 – 2400 cm^{-1} region; the Raman spectra are the most suggestive in this respect.

The deprotonation of the carboxylic group is also supported by the vibrational behavior of the compounds in the 2000 – 1000 cm^{-1} spectral range. According to our previous discussion, the deprotonation of the COOH group gives rise to the anionic COO^- group, which is expected to adopt a C_{2v} symmetry and to reveal the $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ fundamentals.^{5,13} In the case of compounds **3** and **4** (as for all the homologues investigated so far) the first mode may be easily assigned at 1618 – 1587 cm^{-1} . As it concerns the

second fundamental, again, it proved difficult to choose between the many bands crowded in the expected region (1400 – 1200 cm^{-1}).¹³ However, we may tentatively assign the 1310 – 1290 cm^{-1} bands to $\nu_{\text{s}}(\text{COO})$ and/or $\nu(\text{CN})$ modes.

The 2000 – 1000 cm^{-1} spectral range is also relevant for the identity of the heterocyclic unit.^{4,5} Thus, the most important bands for the heterocycle fall in the 1541 – 1515 and 1457 – 1443 cm^{-1} range for the $\nu(\text{C=N})$ fundamental, as well as the 1117 – 1101 and 1059 – 1051 cm^{-1} for the $\nu(\text{N-N})$ and $\nu_{\text{as}}(\text{S-C=S})$ modes, respectively. This interpretation is consistent with the vibrational data reported for d metal homologues⁵ and related mercaptothiadiazoles (i.e. 1510 – 1506 and 1452 – 1450 cm^{-1} for Bismuthiol I).¹⁴ The 1000 – 200 cm^{-1} spectral range shows no unusual features. The bands located in this region were assigned to group bending and other skeleton vibrational modes.

It can be concluded that the deprotonation of the acid **1** takes place at the carboxylic group to generate the carboxylato mono-anion. In addition, the remaining proton is located at a nitrogen atom, which gives option to the thione tautomer form of the heterocyclic unit. These conclusions are in good agreement with the structural data determined for **2** by single-crystal X-ray diffraction.

The structure of **2** consists of discrete dinuclear molecules accompanied by two lattice water molecules each. The two metal centers lay in a slightly distorted octahedral environment described by five oxygen atoms and the S(1) thione sulfur atom of the (3*H*-2-tioxo-1,3,4-thiadiazol-5yl)thioacetato ligand. The proposed coordination geometry is supported by the values of the bond angles centered on sodium [82.98(9) – 99.63(9)°].

The two metal centers are connected through two water bridges and describe all together an almost square four-membered inorganic ring, Na₂O₂ [O(3)-Na(1)-O(3') 87.24(8)°, Na(1)-O(3)-Na(1') 92.76(8)°]. The structural aspects described above favorable compare those found for similar monosodium complexes of mercapto-aza type heterocyclic derivatives (*i.e.* C₃H₂N₃S₃Na·3H₂O).³

The (3*H*-2-tioxo-1,3,4-thiadiazol-5yl)thioacetato ligand shows an un-coordinated and strongly delocalized COO⁻ unit [C-O 1.248(3) - 1.250(3) Å]. The structure of the heterocyclic unit is consistent with the proposed thione tautomeric form. Thus, the C(1)-S(1) bond length of the thione group [1.667(3) Å] suggests the double character of this bond [*cf.* Me₃Sn(PhN₂C₂S₃)₂ C=S: 1.668(3) Å; C₃H₂N₃S₃Na·3H₂O,³ C=S: 1.681(6) Å], while the remaining proton is attached to the neighboring N(1) atom. In addition, the N(1) atom is involved in a longer C-N bond than the N(2) counterpart [C(1)-N(1)1.325(3), C(2)-N(2)1.290(3)Å].

EXPERIMENTAL

Complete physico-chemical and spectroscopic description of the title compounds will be given elsewhere.

Crystallography: Crystallographic data for [Na(C₂N₂HS₃CH₂COO)(H₂O)₄]₂·2H₂O (**2**) are summarized in Table 2. The single-crystal X-ray diffraction analysis was performed on a Bruker SMART APEX system (Babes-Bolyai University of Cluj-Napoca, Romania) using graphite-monochromated Mo-K α radiation (λ = 0.71073 Å). The structure was solved by direct method¹⁵ and refined using SHELX-97.¹⁶ Non-hydrogen atoms were refined anisotropically without exception. Hydrogens were included at calculated positions throughout. An absorption correction (multiscan) was applied.¹⁷ Drawings were created with the MERCURY graphic visualization software.¹⁸

Supplementary material: CCDC reference number 631342. Free information and copies: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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Table 2

Crystallographic data for **2**

Empirical formula	C ₈ H ₂₆ N ₄ O ₁₄ S ₆ Na ₂
Formula weight	640.73
Temperature / K	297(2)
Crystal system; Space group	Triclinic; P-1
a / Å	5.934(2)
b / Å	7.808(3)
c / Å	14.292(5)
α / °	96.733(6)
β / °	91.419(6)
γ / °	95.332(6)
Volume / Å ³	654.4(4)
Z	1
Absorption coefficient / mm ⁻¹	0.621
Reflections collected / unique	7013 / 2670 [R(int) = 0.0379]
Refinement method	Full-matrix least-squares on F ²
Final R indices [I > 2 σ (I)]	R1 = 0.0461, wR2 = 0.0925
R indices (all data)	R1 = 0.0603, wR2 = 0.0981
Goodness-of-fit on F ²	1.053

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