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Dedicated to professor Gh. Marcu at his 80th anniversary

SYNTHESIS AND VIBRATIONAL STUDIES ON NEW COMPLEXES OF MONODEPROTONATED (4*H*-5-MERCAPTO-1,3,4-THIADIAZOL-2-YL)THIOACETIC ACID

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ABSTRACT. Partial neutralisation of (4*H*-5-mercapto-1,3,4-thiadiazol-2-yl)thioacetic acid with 1 eq. of sodium bicarbonate produced the sodium carboxylate salt. This salt was further used in the preparation of the title compounds as four d metal complexes, Co, Ni, Cu and Zn. 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 coordination of the deprotonated carboxylic groups to the metal centers. In all cases, the occurrence of the thione tautomeric form of the heterocycle was found.

Key-words: (4*H*-5-mercapto-1,3,4-thiadiazol-2-yl)thioacetic acid, metal complexes, FT-IR and Raman spectroscopy.

INTRODUCTION

We have an on-going interest in the chemistry of mercapto-aza type heterocyclic derivatives mainly from the aspect of their coordination and supramolecular chemistry, and also because of their various applications in analytical chemistry, materials science, etc.[1-11] Previous structural studies performed on well known analytical reagents revealed their extraordinary potential in this field. For example, 1,3,5-triazine-2,4,6-trithione, $C_3N_3S_3H_3$ (also known as trimercaptotriazine or trithiocyanuric acid) and 4-phenyl-2-mercapto-1,3,4-thiadiazole-5-thione (also known as *Bismuthiol II*) have been intensively used in removing heavy metals from waste waters and also as industrial precursors.[1-6] Recently, the co-crystallization of trithiocyanuric acid with melamine, tricyanuric acid, 4,4'-bipyridine, etc. generated supramolecular structures with nanometric cavities and channels. Many of these compounds have proved excellent zeolitic properties.[7-9] Furthermore, crystallographic investigations on (organo)metallic complexes of such ligands revealed interesting 1D, 2D and 3D supramolecular architectures build up *via* intermolecular covalent and/or secondary interactions.[10,11]

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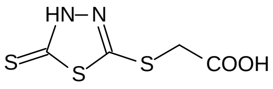
It was concluded that the flat, rigid molecular geometry of the ligands, along with their increased number of heteroatoms E and EH groups (E: O, N, S, etc.), encourage the self-assembly of these molecules into layered channel-type crystal structures. Moreover, the involvement of the NCS groups into the building pattern is crucial.[10,11] For example, the presence of exo- and endocyclic sulfur atoms may give rise to S···S interactions, which have been found of great importance in the supramolecular construction of molecular electronics.[12]

We have recently initiated the vibrational investigation of a new range of π-excessive heterocyclic systems based on dimercapto-thiadiazole, $C_2H_2N_2S_3$ (also known as *Bismuthiol I*).[13,14]

We decided to use one of these compounds, the (4*H*-5-mercapto-1,3,4-thiadiazol-2-yl)thioacetic acid, $C_2HN_2S_3$-CH_2COOH **1** (Scheme 1), in the syntheses of five new metallic derivatives: $M(C_2HN_2S_3\text{-}CH_2COO)_n$, n = 1, M = Na, **2**; n = 2, M = Co, **3**; Ni, **4**; Cu, **5**; Zn, **6**.



Scheme 1

Hence, the aim of this work is the synthesis of the above series of derivatives together with their preliminary IR and Raman characterization. It could infer us about i) the occurrence of the thione *vs.* thiol tautomeric form of the heterocyclic moiety in solid state and ii) to suggest the most probable coordination sites in the series 2-6.

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. Compound **1** was prepared following a literature protocol.[13]

The pure monosodium salt of **1**, $C_2HN_2S_3$-CH_2COONa **2** was obtained by reacting stoechiometric amounts of acid **1** and sodium bicarbonate in aqueous solution, at room temperature and subsequent recrystallization of crude **2** from hot distilled water.

The transition metal complexes of **1** as monodeprotonated forms **3-6**, $[M(C_2HN_2S_3\text{-}CH_2COO)_2]$, M = Co, **3**; Ni, **4**; Cu, **5** and Zn, **6** were synthetised by reacting stoechiometric amounts of **2** with the corresponding metal salt $Co(NO_3)_2\cdot 6H_2O$, $NiCl_2\cdot 6H_2O$, $CuSO_4\cdot 5H_2O$ and $ZnCl_2$, respectively, in aqueous solution, at room temperature. In all cases, the complexes precipitated at once. After stirring the reaction mixtures for 1 – 2 hours, the crude products were filtered and purified by recrystallization from warm distilled water (**3** and **5**) or by washing with warm water (**5** and **6**). Preparation details and brief characterization of compounds **2** – **6** are given in Table 1.

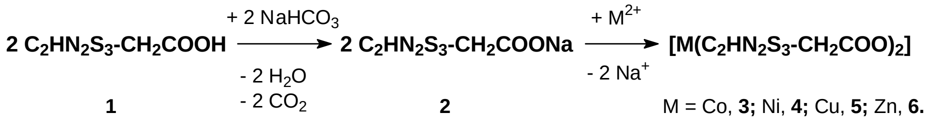
Table 1

Preparation details and characterization of compounds **2** – **6.**

No.	Compound	Yield (%)	mp (°C)	Aspect
2	$C_2HN_2S_3$-CH_2COONa	86	268 - 270	colorless, crystalline
3	$[Co(C_2HN_2S_3\text{-}CH_2COO)_2]$	52	151 - 153	pink , crystalline
4	$[Ni(C_2HN_2S_3\text{-}CH_2COO)_2]$	57	183 - 185	pale green, crystalline
5	$[Cu(C_2HN_2S_3\text{-}CH_2COO)_2]$	58	199 - 201	green, powder
6	$[Zn(C_2HN_2S_3\text{-}CH_2COO)_2]$	52	218 - 220	white, powder

RESULTS AND DISCUSSION

Partial neutralisation of (4*H*-5-mercapto-1,3,4-thiadiazol-2-yl)thioacetic acid, $C_2HN_2S_3$-CH_2COOH **1** with sodium bicarbonate produced the monosodium salt, $C_2HN_2S_3$-CH_2COONa **2**. Compound **2** was further used in the preparation of four d metal complexes, $[M(C_2HN_2S_3\text{-}CH_2COO)_2]$, M = Co, **3**; Ni, **4**; Cu, **5** and Zn, **6** (Scheme 2). All the reactions worked in aqueous media, at room temperature. Compounds **2** – **4** are soluble in water and were isolated as crystalline solids. Compounds **5** and **6** are not soluble in common solvents and were isolated as powders. All metal derivatives are air and light stable in solid state.



$$2\ C_2HN_2S_3\text{-}CH_2COOH \xrightarrow[-\,2\,H_2O \atop -\,2\,CO_2]{+\,2\,NaHCO_3} 2\ C_2HN_2S_3\text{-}CH_2COONa \xrightarrow[-\,2\,Na^+]{+\,M^{2+}} [M(C_2HN_2S_3\text{-}CH_2COO)_2]$$

1 **2** M = Co, **3;** Ni, **4;** Cu, **5;** Zn, **6.**

Scheme 2

The FT-IR and Raman spectra of **2** – **6** were recorded in the 4000 – 400 and 3500 – 200 cm^{-1} spectral ranges, respectively. For the copper(II) complex **5**, 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 our spectral data recorded for **2** – **6** and the known literature data for **1** and *Bismuthiol I*.[13,14]

The 4000 – 2000 cm^{-1} spectral range was relevant for the characterization of NH, OH, SH and CH groups in IR and/or Raman spectra.

Table 2

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

1*		2		3		4		5**	6		Vibrational assign.
IR	Ra	IR	Ra	IR	Ra	IR	Ra	IR	IR	Ra	
-		3487m 3388m		3385s,br		3427- 3385s,br		3448ms 3392m	3449m,br		$\nu(H_2O)$
3100 2500s,br	3103vw	3106w,sh		3090mw		3091mw		3102mw	3102w		$\nu(NH)+\nu(OH)+\nu(CH)$
1693vs	1693m							1705mw	1697w,br		$\nu(C{=}O)+\delta(OH)$
		1604vs	1611vw	1641m 1585vs		1635m 1578vs,br		1603vs	1558vs		$\nu_{as}(COO)$
1494vs 1448mw	1497w 1453vs	1518ms 1454m	1515vw 1457vs	1533s 1444m	1443vs	1533s 1444m	1442vs	1541ms 1452m	1526s,sh 1433ms	1437vs	$\nu(NC)+\delta(NH)$
1407s	1411w	1410s	1406w	1402s	1400w	1402s	1399w	1405m	1410s	1412m	$\delta(CH_2)$
1293s	1303w	1298vs	1290m	1306s	1306s	1306s	1306s	1306s	1333m	1331s	$\nu(C\text{-}O)/\nu_s(COO)$
1120m	1110w	1117m	1110w	1103mw	1108w	1105mw	1105w	1117m	1111mw	1111m	$\nu(NN)$
1051vs	1051s	1053s	1055m	1053s	1059m	1055s	1058m	1053s	1045s	1046m	$\nu_{as}(S\text{-}C{=}S)$
724 s	726w	717m	723w	721m		721m		719m	727m	738w	$\nu_{as}(CSC)_{endo}$
670 m	678s	650w	655s	657w,sh	663s	657w,sh	664s	673w	665w	666s	$\nu_s(CSC)_{endo}$

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.[13,14]

** The Raman spectrum of **5** could not be recorded.

However, the presence of the carboxylic OH group in the starting acid **1** gave rise to a large and complex IR band (approx. 3100 - 2500 cm^{-1}) which overlapped the other expected fundamentals and makes their assignation less accurate. In the IR spectra of **2** - **6**, the title band disappeared as a result of carboxylic group deprotonation. On the other hand, the same spectra show broad bands at 3487 - 3385 cm^{-1} which may be assigned to the $\nu(H_2O)$ mode, as well as weak to medium bands at 3106 – 3090 cm^{-1} which are tentatively assigned to the ν(NH) fundamental.

The Raman spectra of **1** – **6** were more suitable for the interpretation of the tautomeric form of the heterocycle and the characterization of the alkyl fragment. Thus, all spectra lack the characteristic ν(SH) bands, usually assigned in the 2600 – 2400 cm^{-1}. In addition, the $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ stretching vibrations may be clearly assigned at 3022 – 2953 and 2944 – 2905 cm^{-1}, respectively.

It can be concluded that the deprotonation of the acid **1** took place at the COOH group and the ligand participates in coordination as carboxylato anion. In addition, we tentatively suggest that the remaining proton was located at an aza-atom, which gave option to the thione tautomer form of the heterocyclic unit.

The 2000 – 1000 cm^{-1}spectral range was relevant for both heterocyclic and alkyl-carboxylic units of the coordinated ligand. The most important as characteristic bands for the heterocyclic fragment fall in the 1541 – 1433, 1120 – 1103 and 1059 – 1045 cm^{-1} regions and are assigned to the ν(C=N), ν(N-N) and ν_{as}(S-C=S) modes, respectively. The first stretching mode consists of two components, which are assigned in the spectra of **2** - **6** at 1541 – 1515 and 1457 – 1433 cm^{-1}. These components are comparable with the two corresponding fundamentals found for **1** (1494 and 1448 cm^{-1}) and related mercapto-thiadiazoles (e.g. 1510 –1506 and 1452 -1450 cm^{-1} for *Bismuthiol I*). Similarly, the assignment of the other two stretching modes is consistent with the literature data for **1** and *Bismuthiol I*.

As it concerns the alkylcarboxylic substituent, the title spectral range offers consistent information about both CH_2 and COOH groups but the most outstanding behavior was revealed by the COOH / COO$^-$ groups. According to literature,[13-15] the COOH group is defined by two major modes: ν(C=O) and ν(C-OH); the later may be represented by two bands. As the deprotonation occurs, the resulting COO$^-$ group is expected to adopt a C_{2v} symmetry and to reveal the ν_{as}(COO) and ν_s(COO) fundamentals. In the case of compounds **1** – **6**, the first mode of both groups was easily assigned. Thus, for compound **1** the band corresponding to ν(C=O) falls at 1693 cm^{-1} in both IR and Raman spectra while in the spectra of the metal derivatives the same mode is shifted dramatically to lower wave numbers (1641 – 1558 cm^{-1}) and can be related to the ν_{as}(COO) fundamental. The assignment of the ν(C-OH) / ν_s(COO) modes in the expected region (1400 – 1200 cm^{-1}) proved very difficult due to the overlap with a significant number of bands. Despite this ambiguity, we propose a tentative assignment of these fundamentals at 1303 in **1** and 1333 – 1293 cm^{-1} in the series **2** – **6**.

The 1000 – 200 cm^{-1} spectral range shows no unusual features. The plethora of bands located in this region was assigned to group bending and other skeleton vibrational modes (i.e. $\nu_{as}(CSC)_{endo}$ 738 – 717 and $\nu_s(CSC)_{endo}$ 678 – 657 cm^{-1}).

CONCLUSIONS

In the explored series of metal complexes, the ligand (4*H*-5-mercapto-1,3,4-thiadiazol-2-yl)thioacetate is present as carboxylato anion, saving the thione tautomer form. The coordination of the ligand to the metal centers M^{2+} (M = Co, Ni, Cu and Zn) is suspected to occur through the carboxylato group. We avoid, however, to evaluate its coordination behavior by comparing the $\Delta\nu = \nu_{as}(COO) - \nu_s(COO)$ values until more spectral and structural investigations will be completed on the title metal complexes.

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