

Dedicated to the memory of Prof. dr. Ioan Silaghi-Dumitrescu marking 60 years from his birth

SOLID STATE STRUCTURE OF A NEW NICKEL(II) (3*H*-2-THIOXO-1,3,4-THIADIAZOL-2-YL) THIOACETATO COMPLEX

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ABSTRACT. Reaction of the monosodium salt of (3*H*-2-thioxo-1,3,4-thiadiazol-2-yl) thioacetic acid, $\text{Na}(\text{C}_2\text{HN}_2\text{S}_3\text{CH}_2\text{COO})\cdot\text{H}_2\text{O}$ (**1**) with $\text{NiSO}_4\cdot 7\text{H}_2\text{O}$ produced the corresponding nickel(II) complex, $\text{Ni}(\text{C}_2\text{HN}_2\text{S}_3\text{CH}_2\text{COO})_2\cdot n\text{H}_2\text{O}$ where $n = 4$ (**2**) and 6 (**3**). The product was characterized by means of microanalysis and thermal analysis. The crystal structure of **3** was determined by single-crystal X-ray diffraction. The molecular structure consists of discrete molecular units: one octahedral $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ cation and two organic anions, $(\text{C}_2\text{HN}_2\text{S}_3\text{CH}_2\text{COO})^-$. The supramolecular structure of **3** is discussed by comparison with that of **1** in its decahydrate, dinuclear form, $[\text{Na}(\text{C}_2\text{HN}_2\text{S}_3\text{CH}_2\text{COO})(\text{H}_2\text{O})_4]_2\cdot 2\text{H}_2\text{O}$ (**1'**), and reveals the self-assembly of the ionic units into alternating columns through $\text{N}\cdots\text{O}$, $\text{O}\cdots\text{H}\cdots\text{O}/\text{S}$ and $\text{S}\cdots\text{S}$ interactions.

Keywords: mercapto-1,3,4-thiadiazole derivatives; nickel(II) complex; thermal decomposition; crystal structure.

INTRODUCTION

We have an on-going interest in the chemistry of mercapto-aza type heterocyclic compounds (i.e. trithiocyanuric acid, *Bismuthiol I* and *II*), which have been proved valuable candidates for coordination and supramolecular chemistry.¹⁻³ 2,5-Dimercapto-1,3,4-thiadiazole (*Bismuthiol I*, Fig. 1a) displays a flat, rigid molecule with an extensive number of donor atoms which may generate a large variety of coordination and supramolecular patterns, leading in many cases to metallamacrocycles⁴ and metal-organic frameworks (MOFs).^{5,6} In order to improve the flexibility and to increase the coordination versatility

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of the ligand, the *Bismuthiol I* skeleton was symmetrically extended with two carboxylic pedant arms. The resulting (1,3,4-thiadiazole-2,5-diylthio)diacetic acid, $C_2HN_2S_3(CH_2COOH)_2$ (Fig. 1b) was successfully used in its di-anionic form to build new coordination polymers with transition and rare earth metals.⁷⁻¹⁵

Concomitantly, we have initiated structural investigations on the asymmetric homologue, the (3*H*-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetic acid, $C_2HN_2S_3CH_2COOH$ (Fig. 1c) and a large range of coordination and organic derivatives.¹⁶⁻¹⁸

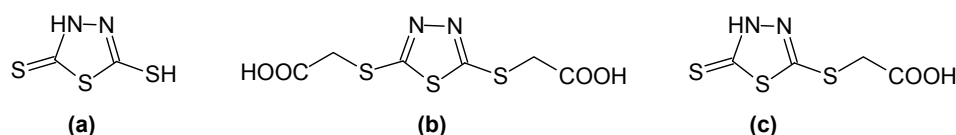


Figure 1. Schematic drawing of *Bismuthiol I* (a), (1,3,4-thiadiazole-2,5-diylthio)diacetic acid (b) and (3*H*-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetic acid (c).

Our choice for asymmetrically substituted *Bismuthiol I* skeleton targets the following objectives: (i) Selective deprotonation of the ligand due to the presence of different acidic groups in the molecule (Fig. 2); (ii) The use of mono-anionic molecule as coordination ligand and/or hydrogen bond donor, which might diversify the self-assembly pattern in solid state; (iii) The use of di-anionic molecule as selective ligand due to the different affinity of the thioamido and carboxylato groups towards metal cations.

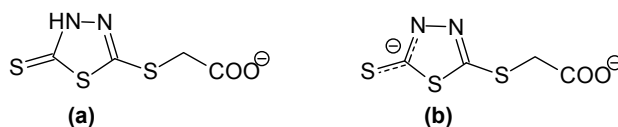


Figure 2. Schematic drawing of the mono- (a) and di-anionic (b) forms of (3*H*-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetic acid.

In the view of the first two objectives, we have reported the general preparative procedure and the vibrational investigation of new metal complexes: $M(C_2HN_2S_3CH_2COO)_n$, $n = 1$, $M = Na$ and K ; $n = 2$, $M =$ group 2 metals, Mn , Co , Ni , Cu and Zn , along with the structural characterization of $[Na(C_2HN_2S_3CH_2COO)(H_2O)_4] \cdot H_2O$.¹⁶⁻¹⁸ The aim of this work is to complete the characterization of the nickel(II) homologue, $Ni(C_2HN_2S_3CH_2COO)_2 \cdot nH_2O$ by means of microanalysis and thermal analysis, as well as single-crystal X-ray diffraction. The supramolecular structure of the title compound is discussed by comparison with that of the starting material in its decahydrate, dinuclear form, $[Na(C_2HN_2S_3CH_2COO)(H_2O)_4]_2 \cdot 2H_2O$ (**1'**). It must be mentioned that the supramolecular structure of **1'** has not been reported previously, along with the molecular structure.¹⁸

RESULTS AND DISCUSSION

The reaction of the monosodium salt of (3*H*-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetic acid, $\text{Na}(\text{C}_2\text{HN}_2\text{S}_3\text{CH}_2\text{COO})\cdot\text{H}_2\text{O}$ (**1**) with $\text{NiSO}_4\cdot 7\text{H}_2\text{O}$ produced the corresponding nickel(II) complex described by the general empirical formula $\text{Ni}(\text{C}_2\text{HN}_2\text{S}_3\text{CH}_2\text{COO})_2\cdot n\text{H}_2\text{O}$ where $n = 4$ (**2**) and 6 (**3**). The hexahydrate product (**3**) is stable only as freshly crystallized solid and turns into the tetrahydrate homologue (**2**) during drying at room temperature. The tetrahydrate product (**2**) shows a much higher stability under ambient conditions, preserving the crystal water.

Thermal analysis: The thermal stability of **2** was checked by thermogravimetric analysis. The simultaneous TG/DTA/DTG curves recorded in N_2 atmosphere are presented in Figure 3.

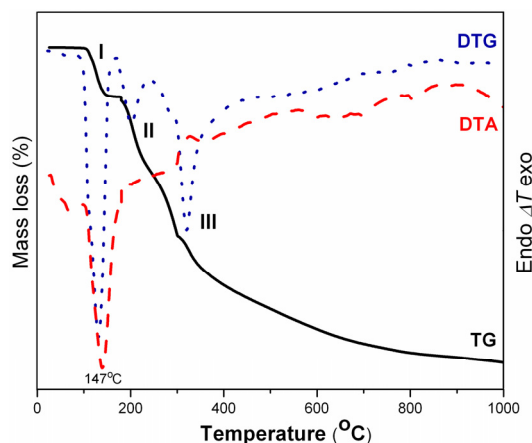


Figure 3. Simultaneous TG/DTA/DTG curves of **2** recorded in N_2 at $10^\circ\text{C}/\text{min}$.

The TG curve shows an initial weight loss (I) of -13.03% in the 100–160°C temperature range, which corresponds to the removal of four water molecules per formula unit (Calc. 13.21%). The DTA peak centred at 147°C reveals the most explicit endothermic process assigned to the dehydration step. Above 180°C the anhydrous complex undergoes a continuous mass loss caused by the decomposition of the organic part, and does not end before 1000°C . The major mass loss occurs in the 200–500°C temperature range revealed by the 205°C (II) and 318°C (III) peaks of the DTG curve. This thermal behaviour is in good agreement with the thermogravimetric analysis reported for Mn(II), Co(II) and rare earth complexes of (1,3,4-thiadiazole-2,5-diylthio)diacetic acid.^{9,10}

For a better elucidation of the decomposition process, the thermogravimetric measurements were repeated in air, coupled with QMS investigation of the evolved gas. The simultaneous TG/DTA and TG-QMS

curves are presented in Figures 4 and 5. Due to the unexpected foaming produced by the energetic decomposition of the complex, the temperature rate was reduced twice, from 10°C to 7.5°C and 5°C, respectively.

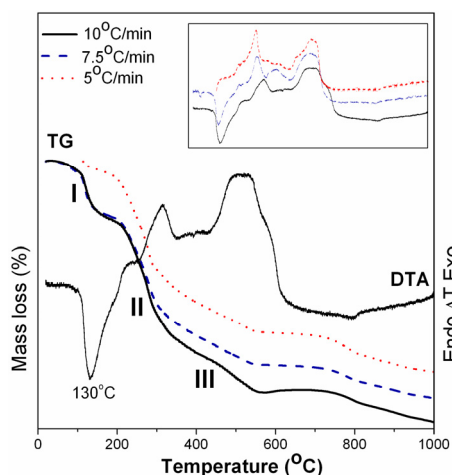


Figure 4. Simultaneous TG/DTA curves of **2** recorded in air at 10, 7.5 and 5°C/min.

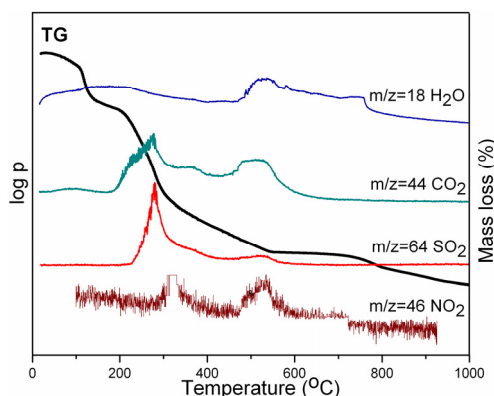


Figure 5. TG-QMS analysis of **2** recorded in air at 7.5°C/min.

The TG/DTA curves recorded at different temperature rates are comparable. However, a slightly decrease in temperature of the DTA peaks can be observed as the temperature rate is reduced.

Similarly to the thermal behaviour in N_2 atmosphere, the first decomposition step in air (I) takes place in the 100–160°C temperature range and corresponds to the complete dehydration of **2** ($4H_2O$, Exp. 13.1–13.3%, Calc. 13.21%) accompanied by an endothermic effect centred at 126–130°C in the DTA plot. The water elimination is confirmed by the broad band of the QMS spectrum located in the mentioned thermal range.

Above 200°C, the anhydrous complex undergoes a complex and continuous mass loss which reveals two major exothermic processes at 281–315 and 509–511°C, respectively in the DTA plots and ends at 550–560°C. The QMS plots reveal the evolution of NO_2 , SO_2 , CO_2 and H_2O , suggesting the combustion of the organic molecules in the 200–550°C range. The overall mass loss of 55% recorded for this temperature range is consistent with the removal of the heterocyclic fragments $C_2HN_2S_2$ (Calc. 42.9%) and part of the pendant chain, C_2H_2 (Calc. 9.5%). The remaining 28.6% solid residue remains stable in the 560–750°C temperature range and may be assigned to $NiSO_4$ (Calc. 28.4%) as a result of the rapid oxidation of the NiS intermediate. Such an oxidation process was proved by running TG/DTA/MS measurements on NiS in O_2 flow.¹⁹

Above 750°C the decomposition continues and does not end before 1000°C. The lack of SO₂ evolution beyond 800°C questions the previous formation of NiSO₄. As a consequence, FT-IR and XRD investigations on the solid residue are in progress and will be published elsewhere.

Structural analysis: The crystal structure of the hexahydrate complex, [Ni(H₂O)₆](C₂HN₂S₃CH₂COO)₂ (**3**) was determined by single-crystal X-ray diffraction. Suitable crystals were freshly crystallized from hot water. The molecular structure is presented in Figure 6 and selected metric data are given in Table 1.

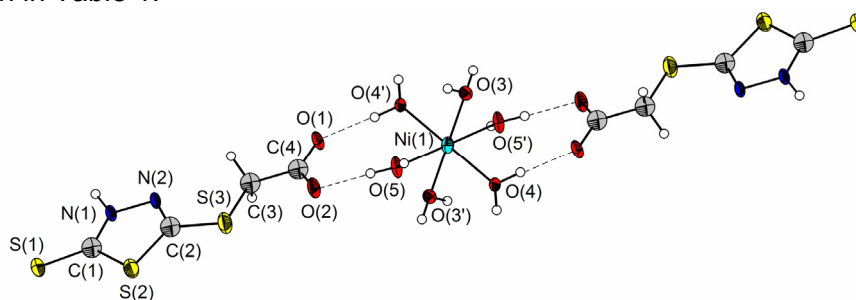


Figure 6. Ortep plot of **3**, showing the labeling used in the text.

Table 1. Selected metric data for **3**.

Bond lengths	[Å]	Bond angles	[deg]
Ni(1)-O(3)	2.054(3)	O(3)-Ni(1)-O(4)	86.37(13)
Ni(1)-O(4)	2.076(3)	O(3)-Ni(1)-O(5)	93.43(14)
Ni(1)-O(5)	2.021(3)	O(4)-Ni(1)-O(5)	90.36(14)
C(1)-N(1)	1.318(6)	C(1)-N(1)-N(2)	118.5(4)
C(2)-N(2)	1.274(6)	C(2)-N(2)-N(1)	109.5(4)
C(1)-S(2)	1.735(5)	C(1)-S(2)-C(2)	88.9(2)
C(2)-S(2)	1.743(4)	N(1)-C(1)-S(2)	108.2(3)
C(1)-S(1)	1.680(4)	N(2)-C(2)-S(2)	114.9(3)
C(2)-S(3)	1.745(4)	C(2)-S(3)-C(3)	98.1(2)
C(4)-O(1)	1.262(6)	O(1)-C(4)-O(2)	126.8(4)
C(4)-O(2)	1.230(6)		

The crystal structure of **3** will be discussed by comparison with that of [Na(C₂HN₂S₃CH₂COO)(H₂O)₄]₂·2H₂O (**1'**), the later being – to the best of our knowledge – the only crystallographic evidence for the (3*H*-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetic moiety.¹⁸ Moreover, the supramolecular structure of **1'** has not been reported previously.

The molecular structure of **3** reveals the presence of three ionic units, a $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ cation and two $(\text{C}_2\text{HN}_2\text{S}_3\text{CH}_2\text{COO})^-$ anions, associated only through O-H \cdots O hydrogen bonding (O \cdots O 2.608 – 2.629 Å, O-H \cdots O 177.29 – 177.39°) designated $R_2^2(7)$. The asymmetric unit of **3** consists of one half of the inorganic complex cation and one organic anion, the remainder being generated by an inversion center located at the metal atom. The structure of the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ unit is largely unexceptional. The nickel(II) cation lays in an octahedral environment described by six water molecules. The very narrow range of the Ni-O bond lengths [2.021(3) – 2.076(3) Å], as well as the almost ideal O-Ni-O bond angles [86.37(13) – 93.43(14)°] support the proposed coordination geometry.

The structure of $(\text{C}_2\text{HN}_2\text{S}_3\text{CH}_2\text{COO})^-$ is comparable with that of the corresponding ligand coordinated to sodium through the S(3) atom in **1'**. Thus, the structure of the heterocyclic unit is governed by the planarity of the dimercapto-thiadiazole skeleton, $\text{C}_2\text{N}_2\text{S}_3$ [Ex. C(1)-N(1)-N(2)-C(2) 1.5(6)°; N(1)-C(1)-S(2)-C(2) -0.2(3)°; S(1)-C(1)-N(1)-N(2) 179.1(3)°; S(3)-C(2)-N(2)-N(1) 179.9(3)°] and the thione tautomeric form of the thiocyanate fragment [C(1)-S(1) 1.680(4) Å]. The later structural feature is supported by comparison with similar CS thione groups in **1'** [1.667(3) Å] and related *Bismuthiol II* complexes [1.653(3) – 1.668(3) Å].² The pendant arm of the organic anion displays an uncoordinated and strongly delocalized carboxylato group [C-O 1.230(6) – 1.262(6) Å]. Despite the expected flexibility, the acetato chain is almost co-planar with the heterocycle [N(2)-C(2)-S(3)-C(3) -11.3(4)°; S(3)-C(3)-C(4)-O(2) 4.5(6)°].

The formation of the 3D supramolecular structure of **3** can be described by three association tendencies: the self-assembly of the organic anions, the self-assembly of the hydrated nickel cations, and the self assembly of the organic / inorganic parts.

The self-assembly of the $(\text{C}_2\text{HN}_2\text{S}_3\text{CH}_2\text{COO})^-$ anions is driven by two distinctive interactions. First, the N(1)-H(1) \cdots O(1) hydrogen bonding [N(1) \cdots O(1) 2.721 Å; N(1)-H(1) \cdots O(1) 170.07°] generates dimer aggregates describing ring patterns which contain a total of 16 atoms, two of them donors and two acceptors, and hence designated $R_2^2(16)$ (Fig. 7a).²⁰ The same motif can be identify in the crystal structure of **1'** [N(1) \cdots O(1) 2.715 Å; N(1)-H(1) \cdots O(1) 178.59°] (Fig. 7b). The dimer aggregates further associate through short S \cdots S interactions, involving the thione S(1) atom in the case of **3** [S(1) \cdots S(1) 3.458 Å] and the S(2)/S(3) atoms in the case of **1'** [S(2) \cdots S(3) 3.420 Å]. Similar S \cdots S interactions (3.45 – 3.71 Å) have been reported for related *Bismuthiol II* complexes.²

The self-assembly of the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ cations in **3** is driven exclusively by water directed hydrogen bonding, leading to columns which run parallel to each other along the a axis (Fig. 8a). The inorganic and organic aggregates are alternatively linked through O-H \cdots O and O-H \cdots S interactions, producing a

three dimensional supramolecular structure. Similarly, the 3D supramolecular structure of **1'** (Fig. 8b) shows hydrated, dinuclear sodium cation columns along the b axis, alternating with the organic aggregates.

Only in this case, the connection between the organic and inorganic parts consists of both O-H...O hydrogen bonding and S→Na coordination.

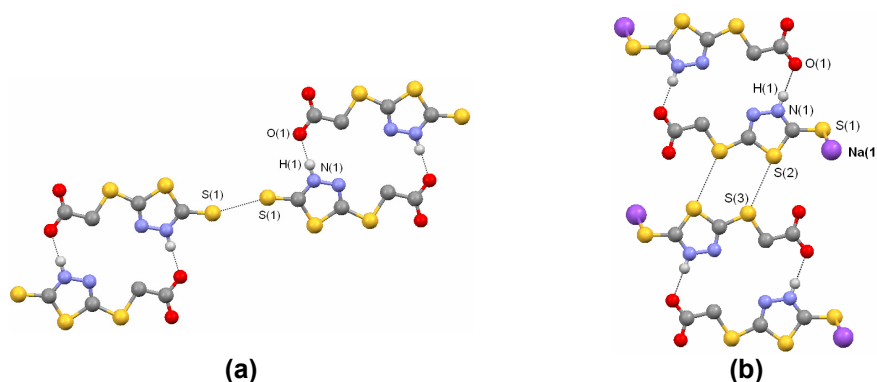


Figure 7. Self-assembly pattern of organic anions in **3** (a) and **1'** (b). Some of the hydrogen atoms were omitted for clarity.

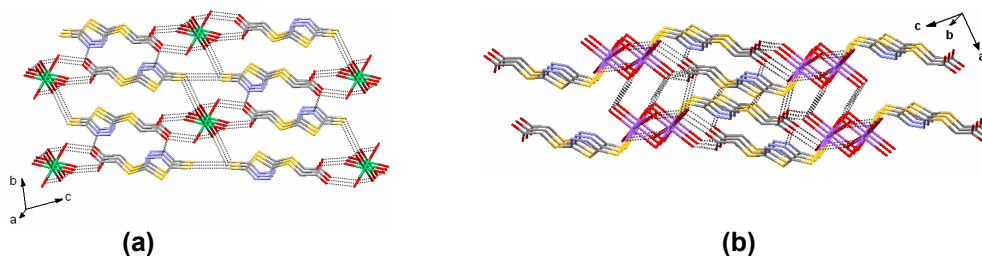


Figure 8. The 3D supramolecular structure of **3** (a) and **1'** (b). Hydrogen atoms were omitted for clarity.

CONCLUSIONS

One new nickel complex of the mono-deprotonated (3H-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetic acid was prepared and characterized in solid state by thermal analysis and single-crystal X-ray diffraction. The thermal decomposition of the tetrahydrate complex was carried out both in N₂ and air atmosphere and revealed the water content, as well as the organic unit combustion. However, none of these measurements were able to prove the formation of nickel chalcogenides below 1000°C. The crystal structure of the hexahydrate complex shows uncoordinated anionic ligands and [Ni(H₂O)₆]²⁺

cations which self-assemble through hydrogen bonding and S...S interactions, generating a 3D supramolecular structure. A similar structural behaviour was evidenced in the crystal structure of the starting material.

EXPERIMENTAL SECTION

Methods and materials

Elemental analyses were obtained on a VarioEL apparatus from Elementar Analysensysteme GmbH. Melting points (uncorrected) were measured in the 30-360°C range using a KRUSS KSPI digital apparatus. Thermal decompositions (TG/DTA/DTG) were carried out using a TGA/SDTA 851-LF 1100 Mettler apparatus. The samples with mass of about 30 mg were placed in alumina crucible of 150 µl and heated non-isothermally from 25°C to 1000°C with a heating rate of 10°C·min⁻¹, under a nitrogen flow of 50 ml·min⁻¹, with the exception of a short isothermal period of 5 min. at 180°C necessary for a better delimitation of decomposition processes. Alternatively, TG/DTA analysis was carried out in air, in the temperature range 20-1000°C, at rates of 5, 7.5 and 10°C/min, coupled with a quadrupole mass spectrometer (QMS) using an atmospheric sampling residual gas analyzer 200 QMS Stanford Research System. Drawings were created with the ORIGIN graphing and data analysis software package.²¹

The inorganic salts were purchased from commercial sources (Merck) as analytical pure substances and were used with no further purification. The preparation of (3*H*-2-thioxo-1,3,4-thiadiazol-5-yl)thioacetic acid was reported elsewhere.²²

Synthesis

Sodium (3H-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetate monohydrate (1). Solid (3*H*-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetic acid (50 g, 0.24 mol) was added in small portions, under continuous stirring, to a clear solution of NaHCO₃ (20.2 g, 0.24 mol / 220 mL H₂O). After the fizzing stopped, the reaction mixture was heated slowly below boiling point to complete the reaction and dissolve the solid material. The resulting hot solution was filtered and cooled to deposit the product as colourless microcrystalline solid, which was further recrystallized from hot distilled water as colourless plates. The product is relatively stable in open atmosphere, at room temperature, as dry solid. In these conditions, it dehydrates continuously until the water content drops to monohydrate. It is soluble in hot water as well as alcohols and dmso. Yield: 47.8 g, 80%; mp: 234-6°C (dec). Microanalysis: found (calc. for C₄H₅N₂S₃O₃Na, MW 248.283) C 19.29 (19.35), H 1.76 (2.03), N 11.09 (11.28).

Nickel(II) (3H-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetate tetrahydrate (2). Aqueous solutions of NiSO₄·7H₂O (0.56 g, 2 mmol / 10 mL H₂O) and Na(C₂N₂HS₃CH₂COO)·H₂O (1 g, 4 mmol / 10 mL H₂O) were stirred at room temperature for 30 minutes. The green precipitate was filtered and further

recrystallized from hot distilled water as green plates. Some of the crystals were suitable for X-ray diffraction analysis. The product is stable in open atmosphere, at room temperature, soluble in hot water and insoluble in common organic solvents. Yield: 0.49 g, 49%; mp: 97-9°C (dec). Microanalysis: found (calc. for $C_8H_{14}N_4S_6O_8Ni$, MW 545,306) C 17.63 (17.62), H 2.23 (2.58), N 9.82 (10.27).

Crystallography

Crystallographic data for $[Ni(H_2O)_6](C_2HN_2S_3CH_2COO)_2$ (**3**) 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 ($\lambda = 0.71073$ Å). The software package SHELX-97 was used for structure solving and refinement.²³ Non-hydrogen atoms were refined anisotropically without exception. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter, except the hydrogen atom of the heterocycle which was found in a difference map and refined with a N–H distance of 0.95(6) Å. Drawings were created with the MERCURY and DIAMOND graphic visualization softwares.^{24,25} **Supplementary material:** CCDC reference number 775075. Free information and copies: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Table 2. Crystal data and structure refinement for **3**.

Empirical formula	$C_8H_{18}N_4O_{10}S_6Ni$
Formula weight	581.33
Temperature / K	297(2)
Crystal system; Space group	Triclinic; P-1
a / Å	4.8707(6)
b / Å	8.2334(10)
c / Å	14.1470(17)
α / °	98.622(2)
β / °	99.405(2)
γ / °	104.016(2)
Volume / Å ³	532.29(11)
Z	1
Absorption coefficient / mm ⁻¹	1.553
Reflections collected / unique	5496 / 2159 [R(int) = 0.0308]
Refinement method	Full-matrix least-squares on F ²
Final R indices [I > 2 σ (I)]	R1 = 0.0589, wR2 = 0.1165
R indices (all data)	R1 = 0.0671, wR2 = 0.1198
Goodness-of-fit on F ²	1.260

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