

CO-CRYSTALLIZATION OF MERCAPTO-1,3,4-THIADIAZOLE DERIVATIVES WITH *ORTHO*-FUNCTIONALIZED PYRIDINES AND SPECTRAL CHARACTERIZATION IN SOLID STATE

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ABSTRACT. Co-crystallization of 2,5-dimercapto-1,3,4-thiadiazole (DMTD) and (3*H*-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetic acid (H₂L) with *ortho*-functionalized pyridines in 1:1 molar ratio produced three molecular complexes: DMTD·2,2'-bipy (1), H₂L·2,2'-bipy (2) and H₂L·2-H₂NPy (3), respectively. The structure of compounds 1–3 was characterized in solid state by microanalysis and FT-IR, FT-Raman and electronic spectroscopy. The spectral data suggest the formation of proton transfer molecular complexes (1) or association products (2, 3). Acid-base C=O···HN and C=O···HO intermolecular interactions are emphasized for compounds 2 and 3.

Keywords: mercapto-1,3,4-thiadiazole derivatives, co-crystallization, spectroscopy

INTRODUCTION

The co-crystallization products have been also named co-crystals and this term has been extensively used as well as criticized in recent years. There were published different interpretations of its meaning, from common multi-component crystals to multiple crystal systems.¹ The latest interpretation was given by Desiraju² who also pointed out the term's ambiguity and recalled that "(...) *it would do one good to remember that we had (and still have) a perfectly good word to describe multi-component crystals, which have specific noncovalent interactions between the distinct molecules, and this is molecular complex*". It is the molecular complex formation and characterization that concerns our present work.

Initially, molecular complexes have been constructed mainly through heteromeric N–H···O, O–H···O and N–H···N hydrogen bonds. Recently, high order systems have been generated through combination of these strong and directional non-covalent connectivities and other interactions, such as halogen-bonding.³

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Our studies in the field of supramolecular chemistry have focused on heterocyclic thione donors containing at least one thioamide group. Compounds such as 2,4,6-trimercaptotriazine (TMT) or mercapto-1,3,4-thiadiazole derivatives (MTD) proved valuable candidates for building supramolecular structures through hydrogen bonding and S...S interactions.^{4,5} In addition, Rao et al. successfully co-crystallized TMT with melamine, tricyanuric acid or 4,4'-bipyridine, engineering channel-type nanostructured crystals. Some of these compounds have proved excellent zeolitic properties.^{6,9} In spite of the plethora of publications discussing co-crystallization of organic acids and bases, there are very few reports on molecular complexes containing MTD moieties. For example, there is one crystallographic evidence concerning the co-crystallization ability of MTD compounds and refers to (4,4'-bipyridine)·(5-amino-1,3,4-thiadiazole-2(3*H*)-thione) in 1:2 ratio.¹⁰

In several of our recent works we reported synthetic procedures and spectral studies on (3*H*-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetic acid, C₂H₂N₂S₃CH₂COOH (H₂L) and related metal complexes. The neutral H₂L consists of a 2,5-dimercapto-1,3,4-thiadiazole, C₂H₂N₂S₃ (DMTD) skeleton extended with one pendant acetic fragment (Fig. 1).

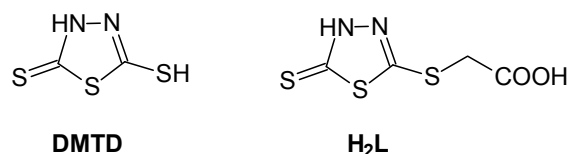


Figure 1. Schematic drawing of 2,5-dimercapto-1,3,4-thiadiazole (DMTD) and (3*H*-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetic acid (H₂L).

Both compounds reveal acidic behaviour. Thus, first step deprotonation of DMTD and H₂L leads to monoanions, which have been identified in metal salts and complexes. The remaining proton is located on the nitrogen¹¹⁻¹³ or sulphur atom¹⁴ in the case of DMTD and on the nitrogen atom in the case of H₂L.¹⁵⁻¹⁷ Further deprotonation of the title acids leads to dianions, also present in several metallic derivatives.

The aim of this work is to study the co-crystallization versatility of H₂L by comparison with that of DMTD using 2-aminopyridine (2-H₂NPy) and 2,2'-bipyridyl (2,2'-bipy) as acceptors. Thus, here we report the preparation of three molecular complexes DMTD·2,2'-bipy (**1**), H₂L·2,2'-bipy (**2**) and H₂L·2-H₂NPy (**3**). The co-crystallization ratio was elucidated by microanalysis. Due to the lack of suitable crystals for single-crystal X-ray diffraction, the structure of the molecular complexes (**1–3**) and the acid-base association was investigated in solid state by FT-IR, FT-Raman, and electronic spectroscopy. Similar studies on molecular complexes containing acceptors of higher symmetry (i.e. *para*-functionalized pyridines), as well as structural studies in solution are in progress.

RESULTS AND DISCUSSION

Co-crystallization of DMTD and H₂L with 2,2'-bipy and 2-H₂NPy in 1:1 molar ratio, produced three molecular complexes: DMTD·2,2'-bipy (**1**), H₂L·2,2'-bipy (**2**) and H₂L·2-H₂NPy (**3**). All the reactions worked in methanol solution, at room temperature or gentle heating. The products are stable during recrystallization from methanol, except compound **1** which shows traces of decomposition products during purification. All complexes are air and light stable in solid state.

The co-crystallization ability of the acids can be roughly estimated from the difference in pK_a between the conjugate acid of the base and the acid. According to literature, the proton transfer should occur for $\Delta pK_a > 3.75$.¹⁸ Taking into account the pK_a values of DMTD (-1.36 and 7.5)¹⁹ and the pK_b values of 2,2'-bipy (9.5 and 14.1) we can predict a single proton transfer from DMTD to 2,2'-bipy ($\Delta pK_a = 5.8$). Unfortunately, no acidity data could be found for H₂L in order to do similar calculations.

The FT-IR and Raman spectra of DMTD, H₂L and the corresponding molecular complexes **1–3** were recorded in solid state, in the 4000–400 and 3500–200 cm⁻¹ spectral ranges, respectively. The spectra of the products are presented in Fig. 2. The most relevant spectral data are listed in Table 1 and 2. Assignments of the starting material vibrational modes were made according to literature data.^{20–24} The vibrational behaviour of DMTD and related compounds was extensively investigated by F. Hipler et al.^{20,21} as both matrix isolated species (IR) and bulk material (Raman). Their assignments support our IR and Raman data recorded for DMTD in solid state. As it concerns the H₂L derivative, we have already reported a brief vibrational characterization²³ and we will use our assignments in further discussions.

DMTD as free and co-crystallized acid: One of the main structural characteristics of DMTD is the co-existence of the thione (HNC=S) and thiol (NC-SH) tautomeric forms in the same molecule, as proved by spectral and crystallographic evidences.^{20,21,25} The thione tautomer of DMTD is characterized in the IR and Raman spectra by the assignment of the $\nu(\text{NH})$ and $\delta(\text{NH})$ vibrational modes. Thus, the IR spectrum of pure DMTD shows a complicated broad feature in the 3200–2700 cm⁻¹ spectral range, characteristic for the $\nu(\text{NH})$ fundamental of poliazolic heterocycles.²² However, the assignment of the $\nu(\text{NH})$ stretching vibration at 3051 cm⁻¹ is in good agreement with literature data.^{20,21} The NH group deformation is well represented by the first two thioamide bands: $\nu(\text{C=N})/\delta(\text{NH})$ (1502 cm⁻¹) and $\delta(\text{NH})$ (1450 cm⁻¹). It is worth mentioning that the position and relative intensity of these bands change significantly in the absence of the thione tautomer.

For example, the spectra of the symmetrically S-substituted derivative 2,5-bis(*tert*-butyldithio)-1,3,4-thiadiazole, reveal only the $\nu(\text{C=N})$ fundamentals in the 1471–1442 cm⁻¹ region.²¹

The IR and Raman spectra of the co-crystallized product (**1**) exhibit the expected $\nu(\text{NH})$ modes in the 3075–3042 cm^{-1} spectral range. However, the assignment of these bands to the thiadiazole and/or – in case of proton transfer – to the pyridinium NH groups is ambiguous.

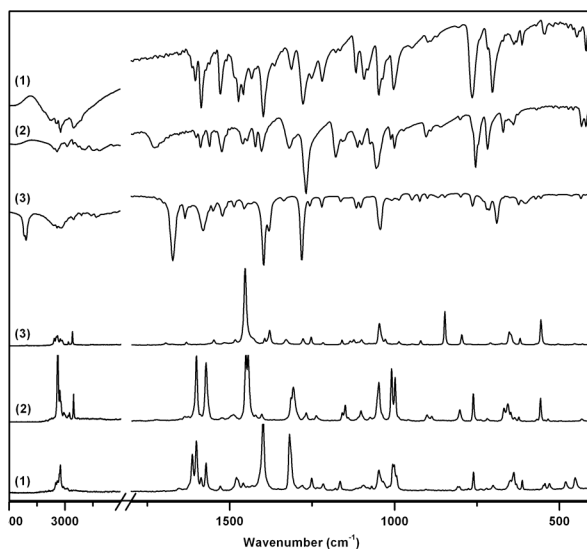


Figure 2. The IR and Raman spectra of DMTD·2,2'-bipy (**1**), H₂L·2,2'-bipy (**2**) and H₂L·2-H₂NPy (**3**).

Table 1. Selected vibrational data (cm^{-1}) for DMTD and DMTD·2,2'-bipy (**1**)

DMTD		DMTD·2,2'-Bipy (1)		Vibrational Assignment
IR	Raman	IR	Raman	
3051 s,br	3056 w	3042 s	3040 ms	$\nu(\text{NH})$
2471 m,br	2489 m,br			$\nu(\text{SH})$
		1587 s	1585 m	$\nu(\text{ring})_{\text{Py}}$
1502 vs	1512 mw	1528 s	1530 w	$\nu(\text{CN}) / \delta(\text{NH})$
1450 m	1453 vs	1472 s	1479 m	$\delta(\text{NH}) + \nu(\text{ring})_{\text{Py}}$
		1457 s	1458 w	
1260 vs	1283 mw	1281 s	1281 mw	$\nu(\text{CN})$
1075 mw	1080 m			$\nu(\text{CS}) / \delta(\text{SH})$
1048 s	1042 m	1047 s	1048 m	$\nu_{\text{as}}(\text{S}=\text{C}-\text{S})$
		1002 s	1006 ms	$\nu(\text{ring})_{\text{Py}}$
939 mw	942 w			$\delta(\text{SH})$
		763 s	761 ms	$\delta(\text{CH})_{\text{Py}}$
712 s	716 w	703 s	701 w	$\nu_{\text{as}}(\text{CSC})$
658 mw	659 vs	640 w	638 ms	$\nu_{\text{s}}(\text{CSC})$

Abbreviations: w – weak, mw – medium weak, m – medium, ms – medium strong, s – strong, vs – very strong, ν – stretching, δ – bending, br – broad, Py – pyridyl ring.

Table 2. Selected vibrational data (cm⁻¹) for H₂L, H₂L-2,2'-bipy (2) and H₂L-2-H₂NPy (3).

H ₂ L ²³			H ₂ L-2,2'-Bipy (2)		H ₂ L-2-H ₂ NPy (3)		Vibrational Assignment
IR	Raman		IR	Raman	IR	Raman	
3093 ms,br	3103 w		3071 m,br	3070 vs	3346 s	3073 m	v(NH ₂)
2950 ms	2953 m		2984 mw	2965 w	3070 m	2975 w	v(NH)
2903s	2915 s		2926 w	2928 m	2939 mw	2939 m	v _{as} (CH ₂)
1693 vs	1693 m		1725 m,br	1724 vw	1672 vs	1697 w	v _s (CH ₂)
					1635 m	1634 w	v(C=O)
			1587 m	1574 vs	1579 s		δ(NH ₂)
1494 vs	1497 w		1561 m		1549 mw	1549 mw	v(ring) _{Py}
			1521 m	1522 w	1522 m	1519 vw	v(CN) / δ(NH)
1448 mw	1453 vs		1460 m	1491 w	1487w	1485 w	v(ring) _{Py}
			1449 m	1446 vs	1454 mw	1456 vs	δ(NH)
			1423 m	1443 vs	1434 w		v(ring) _{Py}
1293 s	1303 w		1269 vs	1270 mw	1281 vs	1279 mw	v(CN)
1051 vs	1051 s		1057 s	1050 s	10413 s	1048 s	v _{as} (S=C-S)
			1002 ms	1001 s	1005 w		v(ring) _{Py}
			754 s	764 ms	764 m	798 m	δ(CH) _{Py}
724 s	726 w		715 m	719 w	719 m	710 w	v _{as} (CSC) _{endo}
670 m	678 s		666 mw	670 m	690 s	654 m	v _s (CSC) _{endo}

Abbreviations: w – weak, mw – medium weak, m – medium, ms – medium strong, s – strong, vs – very strong, br – broad, v – stretching, δ – bending, endo – endocyclic, Py – pyridyl ring.

The same ambiguity may arise from the assignment of the second thioamide band of the acid in the 1479–1457 cm^{-1} region, due to the closeness of the $\nu(\text{C}=\text{N})/\nu(\text{C}=\text{C})$ stretching vibration of the pyridyl ring. On the other hand, the first thioamide band of the co-crystallized DMTD can be clearly located (1528 cm^{-1}) and reveals a positive shift by 26 cm^{-1} when compared to the homologue value of the free acid. This vibrational behaviour may suggest an additional and/or stronger involvement of the NH groups into hydrogen bonding during co-crystallization.²⁴

The thiol tautomer of DMTD is characterized in the IR and Raman spectra by the assignment of the $\nu(\text{SH})$ and $\delta(\text{SH})$ fundamentals. Thus, the spectra of pure DMTD show medium, broad bands assigned to $\nu(\text{SH})$ mode at 2489–2471 cm^{-1} . In addition, the SH group deformation can be found in the 1080–1075 and 942–939 cm^{-1} narrow ranges. The IR and Raman spectra of the co-crystallized product (**1**) do not exhibit any of the previously mentioned bands. As a consequence, the acid may be present in the molecular complex either as thione-thione or thione-thiolate tautomer.

H₂L as free and co-crystallized acid: The donor ability of H₂L is governed by the presence of the thiadiazole heterocycle and the carboxylic group of the pendant arm. Similarly to DMTD, the heterocyclic fragment could exist as thione or thiol tautomer but in this case we have proved that the thione tautomeric form settles in solid state.²³ Thus, it was possible to assign the $\nu(\text{NH})$ fundamental despite the complicate structure of the broad band (3100–2500 cm^{-1}) produced by the carboxylic OH group vibrations. The same $\nu(\text{NH})$ mode was located in the IR and Raman spectra of **2** and **3** around 3070 cm^{-1} , suggesting that the H₂L molecule saves its thione tautomeric form during co-crystallization. In addition, none of the Raman spectra reveals characteristic $\nu(\text{SH})$ bands for the free and co-crystallized acid. This structural feature is even more obvious when we analyse the pattern of the first two thioamide bands. The IR spectrum of the pure H₂L shows a very strong $\nu(\text{C}=\text{N})/\delta(\text{NH})$ band (1494 cm^{-1}) and a medium-to-weak $\delta(\text{NH})$ band (1448 cm^{-1}). In the corresponding Raman spectrum, the two bands switch relative intensities. This spectral feature is very well reproduced by the IR and Raman spectra of **2** and **3** confirming that the heterocycle remains protonated. In addition, the positive shift of the $\nu(\text{C}=\text{N})/\delta(\text{NH})$ mode in the spectra of **2** and **3** by up to 28 cm^{-1} suggests an additional and/or stronger involvement of the NH groups into intermolecular interactions.²⁴

The carboxylic fragment of the pendant chain is best characterized by the $\nu(\text{C}=\text{O})$ vibrational mode assignment at 1693 cm^{-1} as a very strong IR band. The position of this band is significantly shifted in the spectra of the molecular complexes towards higher wavenumbers by 32 cm^{-1} (**2**) or lower wavenumbers by 21 cm^{-1} (**3**). The negative shift of the $\nu(\text{C}=\text{O})$ band does not reach the values reported for the related $\nu_{\text{as}}(\text{COO})$ fundamental (1641–1577 cm^{-1}) in the IR spectra of metallic derivatives containing the acid as carboxylato monanion.^{15–17} As a

consequence, the carboxyl group of H_2L saves its protonated form during co-crystallization. According to literature data, the location of the $\nu(\text{C}=\text{O})$ mode in the approx. $1730\text{--}1700\text{ cm}^{-1}$ region may suggest $\text{C}=\text{O}\cdots\text{H-N}$ interactions, while the location in the approx. $1700\text{--}1660\text{ cm}^{-1}$ region could be the result of $\text{C}=\text{O}\cdots\text{H-O}$ interactions.²⁶ However, the IR spectrum of **3** lacks the medium-to-strong, broad band in the $955\text{--}915\text{ cm}^{-1}$ range, assigned to the $\delta_{\text{op}}(\text{OH}\cdots\text{O})$ mode in carboxylic acid dimmers.²⁴

Ortho-functionalized pyridine acceptors: The IR and Raman spectra of the molecular complexes **1–3** show characteristic frequencies for the 2,2'-bipy and 2- H_2NPy acceptors. Among the most important vibrational modes, the $\nu(\text{ring})$ and $\delta(\text{CH})$ were located in the $1600\text{--}1400$ and $800\text{--}750\text{ cm}^{-1}$, respectively. In addition, the $\nu(\text{NH}_2)$ and $\delta(\text{NH}_2)$ fundamentals of 2- H_2NPy were found in the expected spectral regions. The positive shift of the $\delta(\text{NH}_2)$ modes in the IR spectrum of **3** by 7 cm^{-1} suggests a strengthen of the hydrogen bonds involving this group.²⁴

The electronic spectra of the molecular complexes **1–3** along with those of the corresponding starting materials were recorded in solid state, in the $200\text{--}800\text{ nm}$ spectral range (Fig. 3). The spectra reveal different patterns depending on the nature of the donor acid. Thus, the spectrum of compound **1** consists of a large band which broadens towards visible domain by approx. 100 and 200 nm when compared to the spectra of DMTD and 2,2'-bipy, respectively. Several electronic studies on solutions of molecular complexes and salts containing functionalized pyridinium moieties (i.e. 2- and 4- H_2NPyH^+ , 4,4'-bipy H_2^{2+}) have revealed bathochromic shifts of the UV-bands when compared with those of the neutral pyridine derivatives and donor acids.^{27–30} Moreover, in the case of pyridine-2,6-bis(monothiocarboxylic) acid · 2-aminopyridine proton transfer complex the electronic spectrum shows the formation of a new peak in the longer wavelength domain besides the red-shift of the expected bands.²⁷ In this respect, we can afford to suggest that the electronic behaviour of **1** is a result of the proton transfer from DMTD to 2,2'-bipy and the consequent interaction between the resulting charged species.

On the opposite, the spectra of **2** and **3** show no such significant changes in the shape and position of the initial bands. More specific, the spectrum of **2** consists of a large band ($200\text{--}400\text{ nm}$) which reveals four peaks at 216 , 262 , 304 and 355 nm . These peaks meet their correspondence in the spectra of starting materials, except the 304 nm maximum which seems to mediate the 293 nm transition of H_2L and the 319 nm transition of 2,2'-bipy. Similarly, the spectrum of **3** shows a UV band with four broad maximums at 216 , 239 , 297 , $338\text{--}357\text{ nm}$. These values are also comparable with those found for the starting materials, except the 297 nm maximum which is slightly red-shifted by 4 nm .

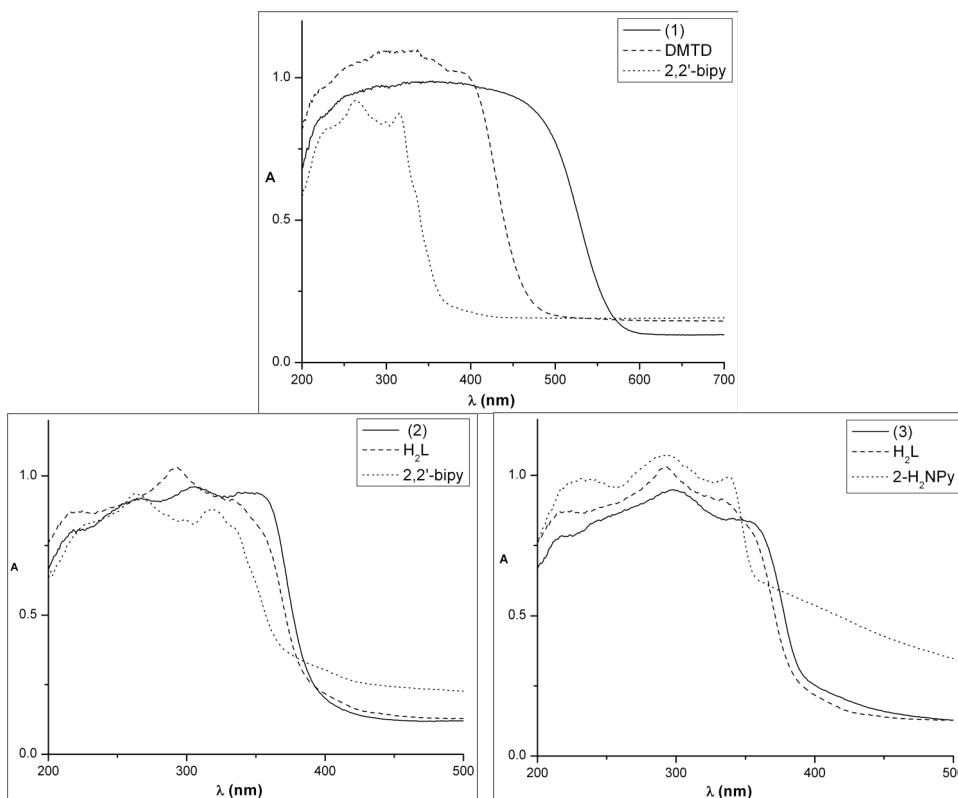


Figure 3. The electronic spectra of DMTD·2,2'-bipy (**1**), H₂L·2,2'-bipy (**2**), H₂L·2-H₂NPy (**3**) and the corresponding starting materials.

CONCLUSIONS

The co-crystallization of DMTD and H₂L with *ortho*-functionalized pyridines in 1:1 molar ratio allows the formation of molecular complexes **1–3**.

The vibrational behaviour of DMTD·2,2'-bipy (**1**) is consistent with the thione-thione or thione-thiolato tautomeric form of the DMTD moiety. Taking into account the major bathochromic shift in the electronic spectrum of **1**, as well as the prediction of the ΔpK_a rule, we suggest an ionic structure containing the thione-thiolato DMTD anion and the monoprotonated 2,2'-bipy cation.

The spectral investigation of H₂L·2,2'-bipy (**2**) and H₂L·2-H₂NPy (**3**) clearly shows that these molecular complexes cannot be the result of a proton transfer, but a simple association process. According to the vibrational data, we may predict different acid-base association scenarios for the two compounds (Fig. 4). Thus, for compound **2** N-H···O hydrogen bonding is suggested between the carbonyl and the NH groups of H₂L. This interaction leaves the possibility

of $N_{Py} \cdots H-O$ connections between the base and the acid. The vibrational data of **3** suggests intermolecular $O-H \cdots O$ hydrogen bonding between the carboxyl groups of neighboring acids. Consequently, the most probable acid-base connection could be the $N-H \cdots N_{Py}$ interaction.

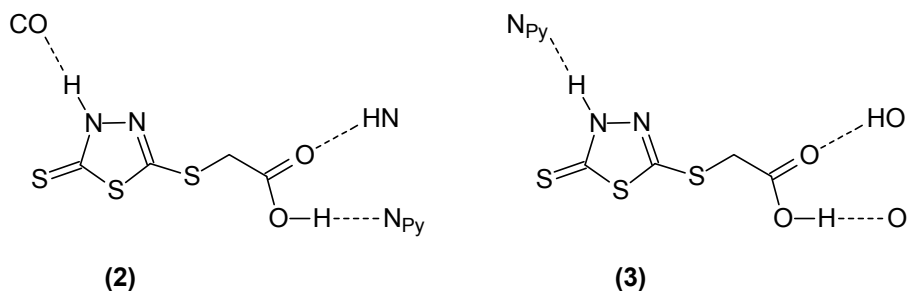


Figure 4. Proposed acid-base association patterns for compounds $H_2L \cdot 2,2'$ -bipy (**2**) and $H_2L \cdot 2-H_2NPy$ (**3**)

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. FT-IR and FT-Raman spectra on solid samples were recorded using a Bruker FT-IR Equinox 55 spectrometer 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 also recorded on KBr pellets using a FT-IR JASCO 600 Spectrometer. The spectral resolution was 2 cm^{-1} . Electronic spectra were recorded on solid samples at room temperature, in the 200–800 nm spectral range, using a Jasco V-670 UV/VIS/NIR spectrophotometer.

The starting materials and solvents were purchased from commercial sources (Merck and Reagents Com.) as analytical pure substances and were used with no further purification or drying. The preparation of (3*H*-2-thioxo-1,3,4-thiadiazol-5-yl)thioacetic acid (**H₂L**) was reported elsewhere.²³

Synthesis: Methanol solutions of donors and acceptors in 1:1 molar ratio were mixed for 30 min. at room temperature (**2** and **3**) or gentle heating (**1**). Compounds **1** and **2** were crystallized from the reaction mixture at low temperature (approx. 5°C). Compound **3** precipitated from the reaction mixture as white powder. Reaction and purification details as well as brief characterization of the products are given below:

2,5-Dimercapto-1,3,4-thiadiazole-2,2'-bipyridyl-CH₃OH (1). The product crystallized from the reaction mixture as orange microcrystalline solid of analytical purity. Recrystallization from methanol shows traces of decomposition products. Yield: 0.57 g, 93%; mp: 120-2°C. Microanalysis: found (calc. for C₁₂H₁₀N₄S₃·CH₄O, MW 338.48) C 46.21 (46.13), H 3.91 (4.17), N 16.96 (16.55).

(3H-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetic acid-2,2'-bipyridyl-0.25H₂O (2). The product recrystallized from MeOH as colorless fine needles. Yield: 0.57 g, 78%; mp: 118-20°C. Microanalysis: found (calc. for C₁₄H₁₂N₄O₂S₃·0.25H₂O, MW 368.978) C 45.46 (45.57), H 3.07 (3.41), N 15.20 (15.18).

(3H-2-thioxo-1,3,4-thiadiazol-2-yl)thioacetic acid-2-aminopyridine (3). The product recrystallized from hot MeOH as colorless fine needles. Yield: 0.57 g, 93%; mp: 226-30°C (dec.). Microanalysis: found (calc. for C₉H₁₀N₄O₂S₃, MW 302.403) C 35.82 (35.75), H 2.87 (3.33), N 18.02 (18.53).

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