# Unexpected Behaviour of Pyridine-2-carbaldehyde Thiosemicarbazonatocopper(II) Entities in Aqueous Basic Medium – Partial Transformation of Thioamide into Nitrile

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Unusual species are obtained from the HL/$Cu^{II}$/$NO_3^-$ system (HL = pyridine-2-carbaldehyde thiosemicarbazone) in basic aqueous solutions. A partial desulfurization process occurs for 1:1 Cu/HL molar ratio which gives rise to the precipitation of the mixed ligand [Cu(L)($L^{CN}$)] (**1**) complex [$HL^{CN}$ = $C_7H_6N_4$, (pyridin-2-ylmethylene)hydrazinecarbonitrile]. This compound contains $Cu^{II}$ ions in a square-pyramidal environment. On the other hand, distorted octahedral [$Cu(L)_2$] (**2**) entities are isolated in excess of the thiosemicarbazone ligand. Desulfurization of the thiosemicarbazone is detected even at physiological pH values. However, this reaction does not take place in absence of $Cu^{II}$ ions, and HL·2.25$H_2O$ (**3**) or HL·$H_2O$ are obtained in these conditions.

## Introduction

The copper(II) derivatives of pyridine-2-carbaldehyde thiosemicarbazone (HL = $C_7H_8N_4S$) exhibit relevant biological properties, in particular related to the cytotoxic effects against tumoral cells.[1] Spectroscopic studies in aqueous solution led to propose the existence of the $[Cu(HL)]^{2+}$, $[Cu(L)]^+$ and [Cu(L)(OH)] species, corresponding to two acid–base equilibria with proton dissociation constants $pK_{a1}$ = 2.40 (deprotonation of the $N_{hydrazinic}$ atom in the ligand) and $pK_{a2}$ = 8.30, respectively.[2] In fact, the high stability of the metal–ligand system has allowed the attainment and structural characterization of several compounds containing $[Cu(HL)]^{2+}$ and $[Cu(L)]^+$ entities.[3] They show a 1:1 metal–thiosemicarbazone stoichiometry, with the thiosemicarbazone acting as an NNS terdentate ligand. However, as far as we are aware, attempts to isolate either the basic [Cu(L)(OH)] species or its derivatives have not been carried out.

The present work deals with the structural studies developed on solids obtained from the pyridine-2-carbaldehyde thiosemicarbazone–nitrate–copper(II) system in aqueous solutions at high pH values. In this way, unexpected [Cu(L)($L^{CN}$)] (**1**) and [$Cu(L)_2$] (**2**) compounds have been obtained [$HL^{CN}$ = $C_7H_6N_4$, (pyridin-2-ylmethylene)hydrazinecarbonitrile] together with the thiosemicarbazone ligand in a new structural arrangement, HL·2.25$H_2O$ (**3**). Surprisingly, we have not found any evidence of the existence of [Cu(L)(OH)] derivatives in the solids isolated.

## Results and Discussion

The addition of sodium hydroxide to an aqueous solution of the Cu(L)($NO_3$) complex at pH = 9–11 yields complex **1** as a major component of a dark brown powdery solid. Unfortunately, attempts to purify this compound have been unsuccessful. In spite of this, it has been possible to obtain some small crystals and to solve the molecular structure[4,5] of the monomeric species, which is shown in Figure 1. As can be seen, one of the thiosemicarbazone ligands in compound **1** is converted into a new carbonitrile derivative which acts as a bidentate ligand. The geometry around the $Cu^{II}$ ions is square-pyramidal ($\tau$ = 0.25).[6] Distances in the NCN terminal moiety are 1.312(8) and 1.129(9) Å for C14–N7 and C14–N8, respectively. The latter is closer to a C≡N link, but the first one exhibits some double bond character. Therefore, cyanamide (N–C≡N) and carbodiimide (N=C=N) contributions must be considered. Furthermore, it must be taken into account the conjugation along all the system. On the other hand, this car-

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bonitrile ligand is unusual from a structural point of view, being the closest related C=N–N–C≡N structure found that corresponding to the C-biphenylene–N(1)-(4-iodophenyl)–N(2)-cyano–azomethinimine compound.[7]

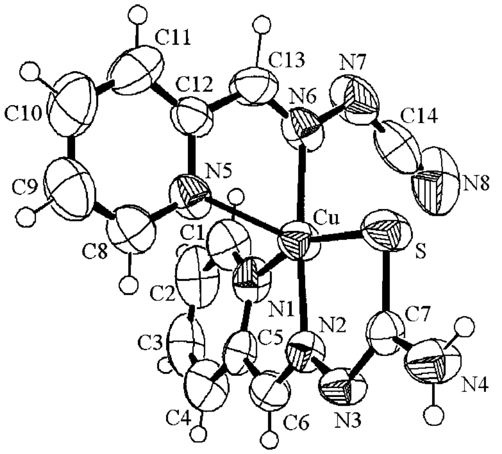


Figure 1. Crystal structure of compound **1**. Selected bond lengths [Å] and angles [°]: Cu–N1 2.025(4), Cu–N2 1.961(4), Cu–S 2.263(2), Cu–N5 2.222(5), Cu–N6 2.039(5), N2–C6 1.288(6), N2–N3 1.351(5), N3–C7 1.330(5), S–C7 1.720(6), N4–C7 1.334(5), N6–C13 1.279(6), N6–N7 1.360(6), N7–C14 1.312(8), N8–C14 1.129(9), N1–Cu–S 159.5(1), N1–Cu–N2 80.7(2), N1–Cu–N6 99.7(2), N5–Cu–N6 78.1(2), N1–Cu–N5 96.0(2), N2–Cu–N6 174.8(2), closest intermolecular Cu···Cu distance 6.528(2)$^{ii}$ ($^{ii}$ = $-x + 1, -y, -z + 1$).

The structure of compound **1** resembles that of complex **2** (see Figure 2) which was prepared with high purity following a 1:2 metal-to-ligand molar ratio in a basic medium.[8] The crystal building of **2** contains isolated distorted octahedral entities where each Cu$^{II}$ ion is bonded to two NNS terdentate thiosemicarbazone ligands. The N1 atom can be considered as pseudocoordinated to the metal centre due to the long Cu–N1 bond length being the topology better described as a [5+1] coordination. Because of the Jahn–Teller effect in the Cu$^{II}$ ion, there are few bis-chelate copper(II) complexes containing terdentate thiosemicarbazone ligands (to the best of our knowledge, less than 5% of the structures reported in the literature).[9]

The desulfurization of the thiosemicarbazone ligand to give the compound **1** is a complex process very sensitive to temperature, pH, time of reaction and stoichiometry. Variations in the experimental conditions at pH values above 7.0 give rise to differences in the composition of the solids. Most of the products obtained in our experiments exhibit very low crystallinity and dark colours. Because of this, it is very difficult to identify the components of the powders. Besides this, the amorphous precipitates show very low solubility in water and other solvents. This fact prevents purification of the samples without inducing important changes in the experimental conditions. All these problems make it necessary to find characteristic parameters to follow the process. In this sense, the strong infrared band at 2108 cm$^{-1}$ corresponding to ν(CN) in compound **1** has allowed us to check the presence of desulfurized species in solid powdered samples obtained at different pH values. EPR measurements have also been used to identify the presence of **1** and **2** in the precipitates. Thus, a degree of desulfurization process has been detected even at physiological pH = 7.4 values in aqueous solutions of Cu(L)($NO_3$) at 40 °C. On the other hand, organic fragments are absent in the black solids collected when the reactions are maintained for more than 1 h at pH = 13 and temperatures higher than 40 °C (IR bands in the 4000–400 cm$^{-1}$ region practically disappear if the products are washed with water after filtering off).

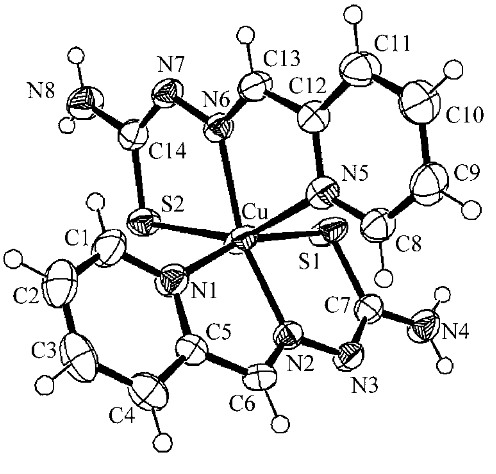
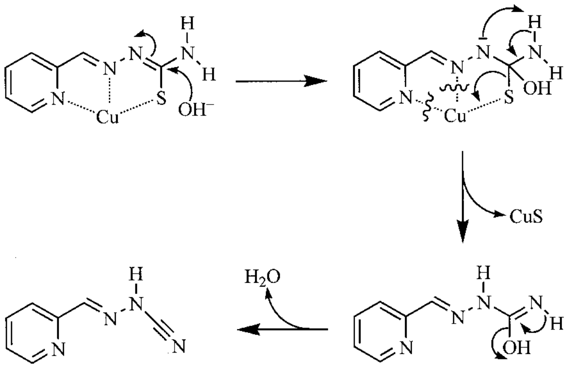


Figure 2. Crystal structure of compound **2**. Selected bond lengths [Å] and angles [°]: Cu–N1 2.515(3), Cu–N2 2.144(3), Cu–S1 2.505(1), Cu–N5 2.059(3), Cu–N6 2.002(3), Cu–S2 2.309(1), N2–C6 1.283(4), N2–N3 1.377(4), N3–C7 1.319(4), S1–C7 1.729(3), N4–C7 1.359(4), N6–C13 1.290(4), N6–N7 1.356(4), N7–C14 1.333(4), S2–C14 1.729(3), N8–C14 1.340(4), N1–Cu–S1 149.61(9), N1–Cu–N2 71.5(1), N1–Cu–N6 84.3(1), N5–Cu–S2 161.83(8), N5–Cu–N6 79.5(1), N1–Cu–N5 85.8(1), N2–Cu–N6 155.7(1), S1–Cu–S2 97.37(4), closest intermolecular Cu···Cu distance 5.9909(7)$^{i}$ ($^{i}$ = $-x + 1, -y + 2, -z + 1$).

A three-step mechanism can be proposed for this reaction (Scheme 1). The resulting HL$^{CN}$ ligand would link to a $[Cu(L)]^+$ entity and deprotonate in basic media. Note that CuS is only a nominal formula to refer the unidentified inorganic species present in the mixture. Nevertheless, qualitative evidences of the presence of sulfide and sulfate have been achieved for some of the samples analysed.[10]



Scheme 1.

Assays using KOH, $NEt_3$, or 0.5 M $Na_2CO_3$/$NaHCO_3$ buffer instead of NaOH lead to similar results. The nitrile derivative is also obtained when Cu(L)($NO_3$) is replaced by $[\{Cu(L)Cl\}_2]$[3b,3c,3i] as starting material.

No evidence of nitrile formation has been found in the absence of $Cu^{II}$ ions, even not when the aqueous solutions were evaporated to dryness. Instead, the yellow $HL{\cdot}2.25H_2O$ (**3**) compound was obtained at pH ≈ 13. The molecular structure of **3**[11] (Figure 3) shows bond lengths and angles very similar to those reported in the literature for $HL{\cdot}H_2O$[12] but, surprinsingly, the *syn* conformation of the N(1) and N(2) atoms with respect to the C(5)–C(6) bond resembles the crystal features of the pyridinium $H_2L^+$ derivatives obtained at very low pH values.[13] On the other hand, evaporation of aqueous solutions of the free ligand at pH ≈ 11 to dryness yields red crystals with the same structure reported by Byushkin et al. for $HL{\cdot}H_2O$ (see Supporting Information).

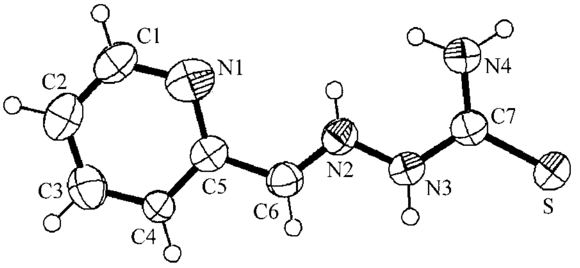


Figure 3. Crystal structure of compound **3**. Selected bond lengths [Å]: N2–C6 1.277(4), N2–N3 1.363(3), N3–C7 1.351(4), S–C7 1.695(3), N4–C7 1.314(4).

Taking into account the extensive literature dealing with the conversion of thioamides and thioureas into carbonitriles, cyanamides and carbodiimides,[14] one could expect that the reaction reported here is also quite common for thiosemicarbazone compounds. However, as far as we are aware, transformation of thiosemicarbazones into carbonitrile derivatives induced by basic media is an unprecedent process. In fact, we have tried the attainment of $HL^{CN}$ by reaction of HL with HgO, but the $[Hg(L)_2]$ compound was obtained.[15] In the same way, previous attempts of desulfurization of HL using $HgCl_2$ + Na in methanol and $Pb(CH_3COO)_2{\cdot}3H_2O$ + KOH in water were unsuccessful.[1j] These results are probably due to the stability that the conjugation induces in this thiosemicarbazone system.

Recently, desulfurization of dithiocarbamatocadmium(II) complexes in the presence of amines has been reported.[16] In addition, there are indirect evidences of desulfurization of an analogous thiosemicarbazonecopper(II) system in aqueous basic medium.[17] However, the reactions described in these papers do not yield carbonitrile derivatives.

The presence of such a process in physiological conditions could lead to a re-interpretation of the biological properties of some thiosemicarbazone systems, mainly those aspects related to the possible therapeutic uses. Furthermore, this reaction opens an inexpensive way to achieve the synthesis of new ligands. In a more general scope, the transformation of thioamides into carbonitriles in the presence of $Cu^{II}$ ions suggests possible pathways for the syntheses of biomolecules in sulfur-rich environments, e.g. prebiotic conditions.[18]

**Supporting Information Available:** IR and EPR spectra, powder diffractograms of samples at different pH values and a summary of the cif output for the $HL{\cdot}H_2O$ compound.

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[1] For instance: a) W. E. Antholine, J. M. Knight, D. H. Petering, *J. Med. Chem.* **1976**, *19*, 339–341; b) W. E. Antholine, J. M. Knight, H. Whelan, D. H. Petering, *Mol. Pharmacol.* **1977**, *13*, 89–98; c) L. A. Saryan, E. Ankel, C. Krishnamurti, D. H. Petering, *J. Med. Chem.* **1979**, *22*, 1218–1221; d) L. A. Saryan, K. Mailer, C. Krishnamurti, W. Antholine, D. H. Petering, *Biochem. Pharmacol.* **1981**, *30*, 1595–1604; e) W. E. Antholine, F. Taketa, *J. Inorg. Biochem.* **1982**, *16*, 145–154; f) W. E. Antholine, F. Taketa, *J. Inorg. Biochem.* **1984**, *20*, 69–78; g) S. B. Padhye, G. B. Kauffman, *Coord. Chem. Rev.* **1985**, *63*, 127–160; h) D. X. West, S. B. Padhye, P. B. Sonawane, *Struct. Bonding* **1991**, *76*, 1–50; i) D. X. West, A. E. Liberta, S. B. Padhye, R. C. Chikate, P. B. Sonawane, A. S. Kumbhar, R. G. Yerande, *Coord. Chem. Rev.* **1993**, *123*, 49–71; j) E. W. Ainscough, A. M. Brodie, W. A. Denny, G. J. Finlay, J. D. Ranford, *J. Inorg. Biochem.* **1998**, *70*, 175–185; k) J. García-Tojal, A. García-Orad, A. Alvarez Díaz, J. L. Serra, M. K. Urtiaga, M. I. Arriortua, T. Rojo, *J. Inorg. Biochem.* **2001**, *84*, 271–278.

[2] a) W. E. Antholine, D. H. Petering, *Proc. Am. Assoc. Cancer Res.* **1974**, *15*, 16; b) D. J. Legget, W. A. E. McBryde, *Talanta* **1974**, *21*, 1005–1011; c) W. E. Antholine, J. M. Knight, D. H. Petering, *Inorg. Chem.* **1977**, *16*, 569–574; d) H. Beraldo, L. Tosi, *Inorg. Chim. Acta* **1986**, *125*, 173–182.

[3] a) C. F. Bell, C. R. Theocharis, *Acta Crystallogr., Sect. C* **1987**, *43*, 26–29; b) A. G. Bingham, H. Bögge, A. Müller, E. W. Ainscough, A. M. Brodie, *J. Chem. Soc., Dalton Trans.* **1987**, 493–499; c) C. F. Bell, K. A. K. Lott, N. Hearn, *Polyhedron* **1987**, *6*, 39–44; d) H. K. Parwana, G. Singh, *Indian. J. Chem.* **1987**, *26A*, 581–583; e) E. W. Ainscough, E. N. Baker, A. M. Brodie, R. J. Cresswell, J. D. Ranford, J. M. Waters, *Inorg. Chim. Acta* **1990**, *172*, 185–190; f) E. W. Ainscough, A. M. Brodie, J. D. Ranford, J. M. Waters, *J. Chem. Soc., Dalton Trans.* **1991**, 1737–1742; g) E. W. Ainscough, A. M. Brodie, J. D. Ranford, J. M. Waters, *J. Chem. Soc., Dalton Trans.* **1991**, 2125–2131; h) E. W. Ainscough, A. M. Brodie, J. D. Ranford, J. M. Waters, K. S. Murray, *Inorg. Chim. Acta* **1992**, *197*, 107–115; i) J. García-Tojal, M. K. Urtiaga, R. Cortés, L. Lezama, T. Rojo, M. I. Arriortua, *J. Chem. Soc., Dalton Trans.* **1994**, 2233–2238; j) J. García-Tojal, J. García-Jaca, R. Cortés, T. Rojo, M. K. Urtiaga, M. I. Arriortua, *Inorg. Chim. Acta* **1996**, *249*, 25–32; k) E. W. Ainscough, A. M. Brodie, J. D. Ranford, J. M. Waters, *J. Chem. Soc., Dalton Trans.* **1997**, 1251–1255; l) J. García-Tojal, L. Lezama, J. L. Pizarro, M. Insausti, M. I. Arriortua, T. Rojo, *Polyhedron* **1999**, *18*, 3703–3711; m) P. Gómez-Saiz, J. García-Tojal, A. Mendia, B. Donnadieu, L. Lezama, J. L. Pizarro, M. I. Arriortua, T. Rojo, *Eur. J. Inorg. Chem.* **2003**, 518–527; n) P. Gómez-Saiz, J. García-Tojal, M. A. Maestro, J. Mahía, L. Lezama, T. Rojo, *Eur. J. Inorg. Chem.* **2003**, 2123–2132; o) P. Gómez-Saiz, J. García-Tojal, M. A. Maestro, J.

Mahía, F. J. Arnáiz, L. Lezama, T. Rojo, *Eur. J. Inorg. Chem.* **2003**, 2639–2650.

[4] Synthesis of **1**: published methods with small modifications were used to synthesize HL[5] and Cu(L)($NO_3$).[3b] The best way that we have found to obtain **1** with a less amount of impurities consists on the dropwise addition of a solution of HL (0.180 g, 1.0 mmol) in water (30 mL) previously basified with 5 M NaOH just to solution of the ligand (pH ≈ 11), to another aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ (0.100 g, 0.5 mmol) with heating (70 °C). Once the addition was completed, the heating was stopped and the reaction was maintained for 1.5 h. The brown precipitate was filtered off, washed with water at pH ≈ 11 (2 × 20 mL) and dried over vacuum. Good results were also obtained starting from Cu(L)($NO_3$) (0.152 g, 0.5 mmol) in water (30 mL) at 80 °C by addition of NaOH 0.1 M to reach pH = 9.0 and further reaction for 1 h maintaining the temperature and pH. Other trials were carried out at different pH values (7.4, 9.0, 11.0, and 13.0), temperatures (40, 50, and 80 °C) and reaction times (1 and 5 h) yielding compounds with varied compositions. **1** is present in some of these solids, except for those obtained in extreme conditions (e. g. reactions for 5 h at 80 °C and any pH value yielded black unidentified amorphous inorganic solids). Brown crystals of **1** suitable for X-ray analysis were separated from the mother liquours of the reaction of $Cu(NO_3)_2{\cdot}3H_2O$ and HL (stoichimetries 2:3) by slow evaporation at room temperature. $C_{14}H_{12}CuN_8S$ (387.92): calcd. C 43.3, H 3.1, N 28.9, S 8.3; found C 40.6, H 3.0, N 26.9, S 7.5. Selected IR bands ($cm^{-1}$, KBr): 3426 w, br., 3290 m, br., 3070 m, br., 3018 w, 2966 w, 2194 vw, 2108 vs, 1646 m, 1596 s, 1526 s, 1483 w, 1468 m, 1446 s, 1427 vs, sh, 1383 s, 1346 m, 1320 m, 1296 w, 1226 s, 1166 vs, 1155 vs, 1016 vw, 897 vw, 880 vw, 766 w, 738 w, 627 w. EPR (X-band, solid sample): room temp. to 120 K, $g_1 = 2.168$, $g_2 = 2.057$, $g_3 = 2.029$. Crystal data: $C_{14}H_{12}CuN_8S$, $M_W = 387.92$, triclinic, space group $P\bar{1}$, $a = 8.119(1)$, $b = 8.678(1)$, $c = 13.761(2)$ Å, $\alpha = 72.97(1)$, $\beta = 85.98(1)$, $\gamma = 62.83(1)°$, $U = 822.4(2)$ Å$^3$, $Z = 2$, $\mu(\text{Mo-}K_\alpha) = 1.468\ mm^{-1}$, $T = 293(2)$ K, 4987 reflections collected, 2496 were unique ($R_{int} = 0.0552$). Final $R$ values, $R1\ [I > 2\sigma(I)] = 0.0527$, $wR2\ [I > 2\sigma(I)] = 0.0574$, $R1$ (all data) = 0.1436, $wR2$ (all data) = 0.0718. CCDC-252369, -252370, and -252371 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[5] F. E. Anderson, C. J. Duca, J. V. Scudi, *J. Am. Chem. Soc.* **1951**, *73*, 4967–4968.

[6] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.

[7] F. Brandl, W. Hoppe, *Z. Kristallogr. Kristallogeom. Kristallchem.* **1967**, *125*, 80.

[8] Synthesis of **2**: A solution containing Cu(L)($NO_3$) (0.152 g, 0.5 mmol) in water (30 mL) was added dropwise with constant stirring to another solution of HL (0.090 g, 0.5 mmol) in water (30 mL) previously basified with NaOH 1 M to pH = 11.0. The reaction mixture was stirred for 2 h at 40 °C. The brown precipitate was filtered off and washed with hot water (2 × 20 mL) and acetone (2 × 20 mL) and dried over vacuum (0.178 g, 84%). Single crystals were obtained from aqueous solutions of HL (in basic medium) and $Cu(NO_3)_2{\cdot}3H_2O$ slowly mixed by means of a diffusion device. $C_{14}H_{14}CuN_8S_2$ (421.99): calcd. C 39.8, H 3.3, N 26.6, S 15.2; found C 39.4, H 3.0, N 26.2, S 15.0. Selected IR bands ($cm^{-1}$, KBr): 3474 m, 3364 w, 3273 m, 3084 m, br., 1627 m, 1614 m, 1600 m, 1590 m, 1548 m, 1477 w, 1406 vs, 1316 m, 1297 m, 1230 m, 1149 s, sh, 1051 w, 883 w, 768 w, 763 w, 732 m, 636 w, 618 w, 516 w, 449 w. EPR (X-band, solid sample): room temp. to 120 K, $g_1 = 2.186$, $g_2 = 2.046$, $g_3 = 2.038$. Crystal data: $C_{14}H_{14}CuN_8S_2$, $M_W = 421.99$, triclinic, space group $P\bar{1}$, $a = 7.810(1)$, $b = 8.695(1)$, $c = 12.993(2)$ Å, $\alpha = 100.508(2)$, $\beta = 92.539(2)$, $\gamma = 102.674(2)°$, $U = 843.0(2)$ Å$^3$, $Z = 2$, $\mu(\text{Mo-}K_\alpha) = 1.559\ mm^{-1}$, $T = 298(2)$ K, 4834 reflections collected, 3345 were unique ($R_{int} = 0.0224$). Final $R$ values, $R1\ [I > 2\sigma(I)] = 0.0435$, $wR2\ [I > 2\sigma(I)] = 0.1170$, $R1$ (all data) = 0.0569, $wR2$ (all data) = 0.1264.

[9] a) P. Souza, A. I. Matesanz, V. Fernández, *J. Chem. Soc., Dalton Trans.* **1996**, 3011–3013; b) M. A. Ali, R. J. Butcher, J. C. Bryan, *Inorg. Chim. Acta* **1999**, *287*, 8–13; c) M. A. Ali, A. H. Mirza, A. M. S. Hossain, M. Nazimuddin, *Polyhedron* **2001**, *20*, 1045–1052.

[10] Qualitative tests used to detect the presence of (a) sulfide and (b) sulfate: (a) HCl(c) (0.5 mL) was added to 0.030 g of each sample in a test tube, being the top of the tube covered with a paper wet with a solution of $Pb(NO_3)_2$ 0.5 M. $H_2S$ evolution leads to the PbS formation; (b) addition of HCl(c) (1.0 mL) to 0.030 g of the solid, filtration, and addition of $Ba(NO_3)_2$ 0.04 M (0.5 mL) to the acid solution. White $BaSO_4$ precipitates if sulfate ions are present.

[11] Synthesis of **3**: several drops of 5 M NaOH were added to a suspension of HL (0.180 g, 1 mmol) in water (20 mL) to reach a pH ≈ 13 with heating. Some minutes later, the solid disappeared leading to a pale yellow solution. The reaction mixture was allowed to react 1 h after which a white crystalline compound was filtered off, washed with water at basic pH (2 × 20 mL) and dried (0.132 g, 60%). Pale yellow crystals suitable for X-ray studies were separated from a solution of HL in water at pH ≈ 13. $C_7H_{12.5}N_4O_{2.25}S$ (220.77): calcd. C 38.1, H 5.9, N 25.4, S 14.5; found C 38.3, H 5.4, N 25.2, S 14.7. Selected IR bands ($cm^{-1}$, KBr): 3457 m, br., 3350 s, sh, 3189 m, sh, 3045 w, 2956 w, br., 2804 w, br., 1616 s, 1603 m, 1590 s, 1566 m, 1540 vs, br., 1488 w, 1467 vs, 1433 s, 1360 s, 1285 vs, 1249 s, sh, 1152 m, 1113 s, 1090 m, 1066 m, 1051 m, 998 m, 940 m, 900 w, 880 m, 812 m, 775 m, 745 m, 546 m, br., 623 m, 555 w, 518 w, 452 w, 419 w. $^1$H NMR (400 MHz; [D$_6$]acetone, 25 °C), $\delta$ = 10.72 (s, 1 H, NH), 8.58 (d, $^3J_{H,H}$ = 5 Hz, 1H, 1-H), 8.21 (s, 1 H, 6-H), 8.17 (d, $^3J_{H,H}$ = 8 Hz 1 H, 4-H), 8.04 (s, 1 H, $NH_{terminal}$), 7.8 (m, 1H, 3-H), 7.62 (s, 1 H, $NH_{terminal}$), 7.36 (m, 1 H, 2-H). Crystal data: $C_7H_{12.5}N_4O_{2.25}S$, $M_W = 220.77$, tetragonal, space group $I4_1/a$, $a = b = 13.6755(8)$, $c = 22.122(2)$ Å, $\alpha = \beta = \gamma = 90°$, $U = 4137.3(5)$ Å$^3$, $Z = 16$, $\mu(\text{Mo-}K_\alpha) = 0.298\ mm^{-1}$, $T = 293(2)$ K, 11986 reflections collected, 2124 were unique ($R_{int} = 0.0404$). Final $R$ values, $R1\ [I > 2\sigma(I)] = 0.0593$, $wR2\ [I > 2\sigma(I)] = 0.1827$, $R1$ (all data) = 0.0788, $wR2$ (all data) = 0.2018.

[12] V. N. Byushkin, Y. M. Chumakov, N. M. Samus, I. O. Baka, *Zh. Strukt. Khim.* **1987**, *28*, 140–142.

[13] a) M. K. Urtiaga, M. I. Arriortua, J. García-Tojal, T. Rojo, *Acta Crystallogr., Sect. C* **1995**, *51*, 2172–2174; b) A. Morsali, A. Ramazani, F. Jamali, F. Gouranlou, *Z. Kristallogr. New Cryst. Struct.* **2001**, *216*, 607–608.

[14] For instance: a) W. Weith, *Ber. Dtsch. Chem. Ges.* **1873**, *6*, 1389; b) F. Kurzer, *J. Chem. Soc.* **1949**, 3033–3038; c) F. Kurzer, K. Douraghi-Zadeh, *Chem. Rev.* **1967**, *67*, 107–145; d) H. Ulrich, A. A. R. Sayigh, *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 704–712; e) K. Friedich, K. Wallenfels, *Isonitrile Chemistry*, I. Ugi Academic, New York, **1971**; f) X. Shen, X. Shi, B. Kang, Y. Tong, Y. Liu, L. Gu, Q. Liu, Y. Huang, *Polyhedron* **1999**, *18*, 33–37; g) L. Kovacs, E. Ösz, Z. Györgydeák, *Carbohydr. Res.* **2002**, *337*, 1171–1178; h) O. López, I. Maya, V. Ulgar, I. Robina, J. Fuentes, J. G. Fernández-Bolaños, *Tetrahedron Lett.* **2002**, *43*, 4313–4316; i) J. C. Manimala, E. V. Anslyn, *Eur. J. Org. Chem.* **2002**, 3909–3922; j) Y.-M. Zhang, L. Xian, T.-B. Wei, K.-B. Yu, *J. Chem. Research (S)* **2003**, *798*–799; k) E. V. Kudrik, A. Theodoridis, R. van Eldik, S. V. Makarov, *Dalton Trans.* **2005**, 1117–1122, and references therein.

[15] Drops of 5 M NaOH were added over a solution of $HgCl_2$ (0.070 g, 2.5 mmol) in water (30 mL) just to complete precipitation of yellow HgO, which was filtered off and washed with water (2 × 20 mL) and acetone (20 mL). The freshly prepared oxide was put into a flask with a small amount of acetone and HL (0.180 g, 1 mmol) was added dropwise. The reaction was kept with reflux for 5 h. A yellow solid was collected and

washed with acetone (20 mL). This compound is a mixture of $[Hg(L)_2]$ + HgO. For a complete characterization of $[Hg(L)_2]$, see ref.[1j]

[16] L. H. Van Poppel, T. L. Groy, T. Caudle, *Inorg. Chem.* **2004**, *43*, 3180–3188.

[17] P. Gómez-Saiz, J. García-Tojal, V. Díez-Gómez, R. Gil-García, J. L. Pizarro, M. I. Arriortua, T. Rojo, *Inorg. Chem. Commun.* **2005**, *8*, 259–262.

[18] F. Duvernay, T. Chiavassa, F. Borget, J.-P. Aycard, *J. Am. Chem. Soc.* **2004**, *126*, 7772–7773.

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