






Proceeding Paper

Design, Synthesis and Structural Study of a Bisthiosemicarbazone Ligand Precursor of Metallosupramolecular Architectures [†]

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Abstract: The increase in the investigation of different self-assembled architectures derived from thiosemicarbazone ligands can be attributed to the numerous functional metallosupramolecular architectures with practical applications that can be obtained. The potentially tetradentate organic bisthiosemicarbazone ligand H₂L possesses two flexible bidentate [NS] domains separated by a short and rigid spacer, which could stabilize several metal ions and thus different metallosupramolecular architectures. H₂L was prepared by the reaction between two equivalents of N-ethylhydrazinecarbothioamide and one equivalent of 1,1',1''-(benzene-1,3,5-triyl)tris(ethan-1-one) and was fully studied using several techniques, including X-ray diffraction.

Keywords: bisthiosemicarbazone; ligand; metallosupramolecular architectures



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1. Introduction

In recent decades, thiosemicarbazone compounds and their derived metal complexes have attracted particular interest due to their diverse biological properties that they exhibit such as antioxidant [1], antimicrobial [2,3] and cytotoxic activities [4,5]. Moreover, bisthiosemicarbazones are versatile organic compounds due to the several donor atoms that are present in their skeleton. For this reason, this type of organic compound is widely used in the field of Coordination Chemistry with the aim of obtaining metal complexes with diverse applications [6,7].

Our research group has broad experience in using bisthiosemicarbazone skeletons to obtain different metallosupramolecular architectures [8,9]. To deepen the study of these architectures, herein we report the design, synthesis and structural characterization of a bisthiosemicarbazone ligand named H₂L containing a short and rigid spacer that could be a precursor of helicate- and mesocate-type metallosupramolecular architectures.

2. Experimental Section

2.1. Reactants and Solvents

All solvents, 1,3,5-triacetylbenzene and 4-N-ethyl-3-thiosemicarbazide are commercially available and they were used without further purification.

2.2. Synthesis and Characterization of the Bisthiosemicarbazone Ligand H₂L

The bisthiosemicarbazone ligand H₂L was prepared by reaction between one equivalent of 1,3,5-triacetylbenzene and two equivalents of 4-N-ethyl-3-thiosemicarbazide (Figure 1).

First, 0.502 g (2.46 mmol) of 1,3,5-triacetylbenzene and 0.5864 g (4.92 mmol) of 4-*N*-ethyl-3-thiosemicarbazide was solved in absolute ethanol (ca. 50 mL) using *p*-toluenesulfonic acid as catalyst. The solution was refluxed under magnetic stirring for 4 h and the resulting solution was evaporated (to a volume of ~20 mL) and cooled to 4 °C until the formation of a yellow solid was observed. This solid was filtered off and then washed with diethyl ether. Yield: 0.868 g (87%) elemental analysis, % theoretical ($C_{18}H_{26}N_6OS_2$): C, 53.17; H, 6.45; N, 20.67; S, 15.77; % experimental: C, 50.84; H, 6.64; N, 21.34; S, 15.38; IR spectroscopy (KBr, cm^{-1}): $\nu(N-H)$ 3238, $\nu(C=N)$ 1644, $\nu(C=O)$ 1715, $\nu(C=S)$ 1108 and 763; mass spectrometry (ESI+, m/z): 407.46 [$H_2L + H$] $^+$; 1H NMR [DMSO]: 10.12 (s, 2H), 8.18 (d, 2H, $J = 2.3$ Hz), 7.81 (t, 2H, $J = 3.0$ Hz), 7.68 (t, 2H, $J = 8.6$ Hz) 3.51 (m, 4H), 2.01 (s, 6H), 1.53 (t, 6H, $J = 6.2$) ppm.

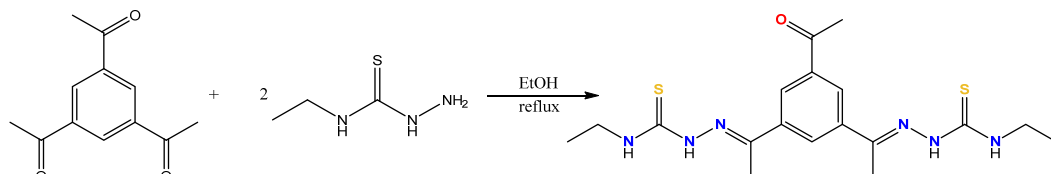


Figure 1. Synthesis of the bithiosemicarbazone ligand H_2L .

2.3. Crystallographic Data of H_2L

H_2L : $C_{18}H_{26}N_6OS_2$; MW: 406.59 $g \cdot mol^{-1}$; crystal dimensions 0.24 \times 0.16 \times 0.14 mm; triclinic; P1; $a = 7.4598$ (2), $b = 11.3924$ (3), $c = 96.113$ (2) Å; $\alpha = 96.113$ (2); $\beta = 101.988$ (10), $\gamma = 98.77$ (2) °; $V = 989.45$ (9) Å 3 ; $z = 2$; $\mu = 0.29$ mm $^{-1}$; measured reflections = 14,923; independent reflections [R_{int}] = 2770 [0.043]; $R = 0.055$; $wR = 0.139$.

The main bond distances and angles (Table 1) are within the expected ranges for thiosemicarbazone-derived ligands [10].

Table 1. Selected bond length and angles for ligand H_2L .

Main Bond Distances (Å)			
O1-C17	1.220 (3)	N3-C9	1.323 (4)
N1-C8	1.289 (3)	N3-C10	1.457 (4)
N1-N2	1.383 (3)	N4-C13	1.277 (4)
N2-C9	1.362 (3)	N4-N5	1.371 (3)
N5-C14	1.370 (4)	N6-C14	1.378 (13)
N6-C15	1.496 (16)	S1-C9	1.629 (3)
S2-C14	1.678 (3)		
Angles (°)			
C8-N1-N2	117.1 (2)	C13-N4-N5	119.9 (3)
C9-N2-N1	119.2 (2)	N5-C14-N6	113.6 (6)
N3-C9-N2	117.2 (2)	N6-C14-N5	117.8 (7)
N2-C9-S1	118.8 (2)	N5-C14-S2	118.9 (3)
N3-C9-S1	124.2 (2)	N6-C14-S2	126.4 (6)
C14-N4-N5	118.6 (3)		

3. Results and Discussion

The potentially dianionic and tetradentate bithiosemicarbazone ligand H_2L displays two flexible bidentate [NS] binding domains separated by a short and rigid benzene-derived spacer (Figure 2).

The ligand was obtained by reaction between 1,3,5-triacetylbenzene and 4-*N*-ethyl-3-thiosemicarbazide in a 1:2 molar ratio, as described in the Experimental Section. The solid product obtained was fully characterized by several techniques. Slow evaporation of the mother liquors from the synthesis of H_2L in absolute ethanol allowed us to obtain good-quality crystals for monocrystal X-ray studies. The crystal structure consists of discrete molecules that crystallize in the triclinic P1 system (Figure 3).

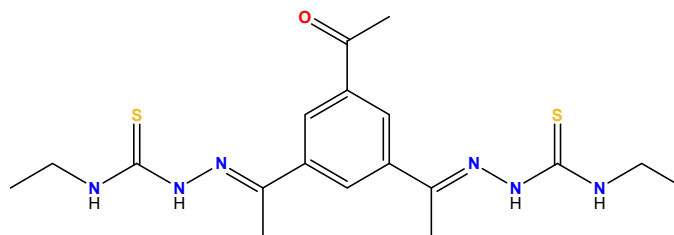


Figure 2. Bithiosemicarbazone ligand H₂L.

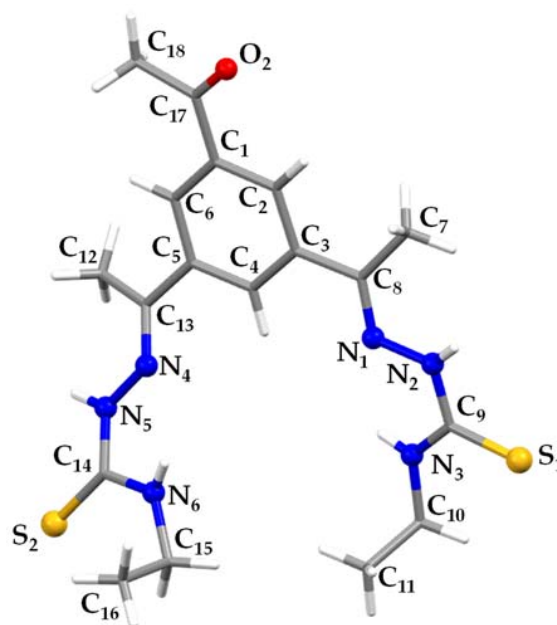


Figure 3. Crystal structure of H₂L.

The thiosemicarbazone arms adopt a *syn-close* arrangement with both branches directed to the same side and an *E* conformation in relation to the imine bonds. Thus, the sulfur and nitrogen donor atoms (N1/S1 and N4/S2) are oriented in opposite directions requiring a change in the conformation to form metallosupramolecular helicate- or mesocate-type architectures. The bond distances and angles are in the order of those normally found in thiosemicarbazone ligands and do not merit further discussion.

4. Conclusions

The bithiosemicarbazone ligand H₂L has been successfully synthesized with high purity and yield. Its crystal structure shows that the sulfur and nitrogen donor atoms are oriented in opposite directions in both arms, indicating the need for conformational rotation to coordinate to metal ions and further obtain helicate- and mesocate-type metallo-supramolecular architectures.

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