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Proceeding Paper

Design, Synthesis and Structural Study of a *Bis*thiosemicarbazone Ligand Precursor of Metallosupramolecular Architectures †

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Abstract: The increase on 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 *bis*thiosemicarbazone ligand H_2L possesses two flexibles bidentate [NS] domains separated by a short and rigid spacer, which could stabilize several metal ions and thus different metallosupramolecular architectures. H_2L has been prepared by 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 by using several techniques, including X-ray diffraction.

Keywords: *bis*thiosemicarbazone; ligand; metallosupramolecular architectures

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1. Introduction

Over the last 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, *bis*thiosemicarbazones are versatile organic compounds due to the several donor atoms that present in their skeleton. For this reason, this type of organic compounds 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 a broad experience using *bis*thiosemicabazone sketetons 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 *bis*thiosemicarbazone ligand named H_2L containing a short and rigid spacer (Figure 2) that could be 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 ant they were used without further purification.

2.2. Synthesis and Characterization of the Bisthiosemicarbazone Ligand H$_2$L

The *bis*thiosemicarbazone ligand H$_2$L has been prepared by reaction between one equivalent of 1,3,5-triacetylbenzene and two equivalents of 4-*N*-ethyl-3-thiosemicarbazide (Figure 2). First, 0.502 g (2.46 mmol) of 1,3,5-triacetylbenzene and 0.5864 g g (4.92 mmol) of 4-*N*-ethyl-3-thiosemicarbazide were solved in absolute ethanol (*ca.* 50 mL) using p-toluensulfonic 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}): ν(N-H) 3238, ν(C=N) 1644, ν(C=O) 1715, ν(C=S) 1108 and 763; mass spectrometry (ESI+, *m*/*z*): 407.46 [H$_2$L + H]$^+$; ^{1}H 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.

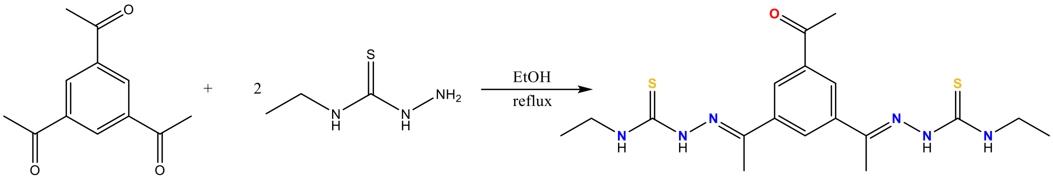

Figure 1. Synthesis of the *bis*thiosemicarbazone ligand H$_2$L.

2.3. Crystallographic Data of H$_2$L

H$_2$L: $C_{18}H_{26}N_6OS_2$; *MW:* 406.59 g·mol^{-1}; crystal dimensions 0.24 × 0.16 × 0.14 mm; triclinic; P1; *a* = 7.4598 (2), *b* = 11.3924 (3), *c* = 96.113 (2) Å; *α* = 96.113 (2); β = 101.988 (10), γ = 98.77 (2) ^{0}; V = 989.45 (9) Å^3; z = 2; μ = 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$_2$L.

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)	N6-14	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 *bis*thiosemicarbazone ligand H$_2$L diplays two flexibles bidentate [NS] binding domains separated by a short and rigid bencene-derived spacer (Figure 2).

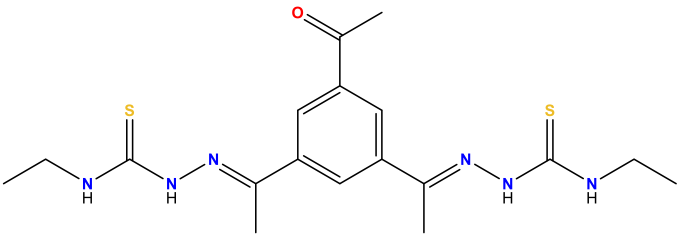

Figure 2. *Bis*thiosemicarbazone ligand H_2L.

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).

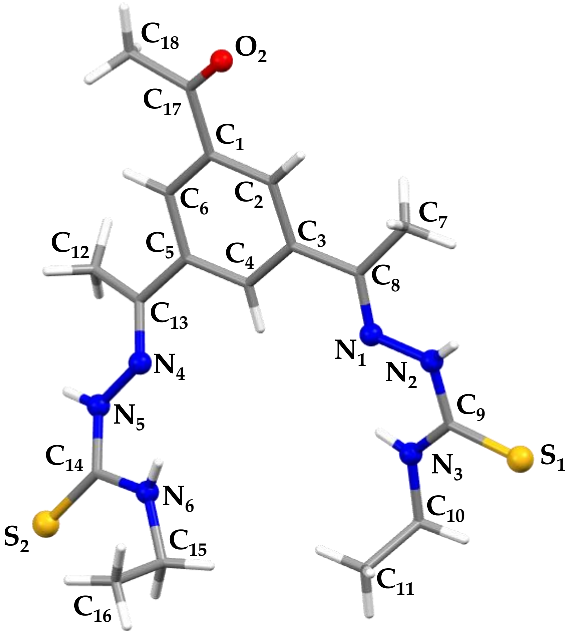

Figure 3. Crystal structure of H_2L.

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 *bis*thiosemicarbazone ligand H_2L has been successfully synthesized with high purity and yield. It crystal structure shows that the sulfur and nitrogen donor atoms are oriented in opposite directions in both arms, indicating the needed of a conformational rotation to coordinate to metal ions and further obtain helicate and mesocate-type metallosupramolecular architectures.

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