



NOTE

Synthesis and Characterization of 1,10-Phenanthroline-2,9-dicarbaldehyde-*bis*-(thiosemicarbazone)

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In this work, 1,10-phenanthroline-2,9-dicarbaldehyde-*bis*-(thiosemicarbazone) having N and S donor atoms has been synthesized and characterized by ¹H NMR, IR and mass spectroscopy. Having *bis*-(thiosemicarbazone) on phenanthroline ring, it should be considered as a useful ligand in coordination chemistry.

Key Words: Multidentate ligand, Thiosemicarbazone, 1,10-Phenanthroline-2,9-dicarbaldehyde, Spectral studies.

1,10-Phenanthroline derivatives have been widely used as ligands in both analytical and coordination chemistry¹. Moreover, most of the works on these ligands have been prompted by the intense current interest in their catalytic, complexation and diverse biological activities^{2,3}.

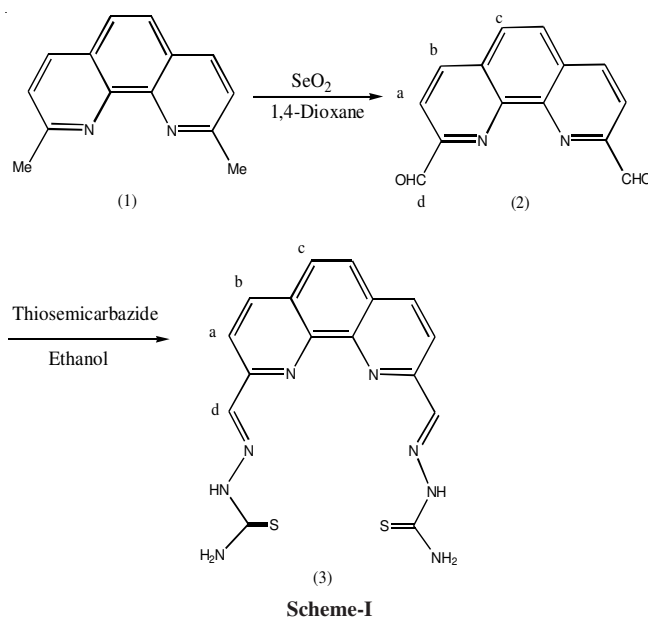
In the area of inorganic chemistry thiosemicarbazide (TSC), ¹NH₂-²NH-C(S)-³NH₂, behaves as a bidentate ligand coordinated through the terminal ¹N and S atoms⁴ and they form highly stable and intensely coloured complexes which are used for spectrophotometric determination of metal ions in different media⁵. Besides, thiosemicarbazides and their derivatives have become the subjects of innumerable studies because of their captivating biological activities⁶⁻⁹.

As part of our research, we reported the synthesis and spectroscopic characterization of 1,10-phenanthroline-2,9-dicarbaldehyde-*bis*-(thiosemicarbazone).

2,9-Dimethyl-1,10-phenanthroline (neocuproine) served as a starting material for the synthesis of the multidentate thiosemicarbazone ligand (**Scheme-I**). Selenium dioxide oxidation of neocuproine (**1**) afforded 1,10-phenanthroline-2,9-dicarbaldehyde (**2**). Subsequent reaction of (**2**) with thiosemicarbazide, afforded 1,10-phenanthroline-2,9-dicarbaldehyde-*bis*-(thiosemicarbazone) (**3**) in good yield (**Scheme-I**).

All chemicals and solvents used in this study were purchased from Merck chemical. Melting points were determined on a Kofler hot stage apparatus and are uncorrected.

The IR spectra were obtained on a Shimadzu 470 spectrophotometer (potassium bromide disks). ¹H NMR spectra was recorded using a Varian 400 spectrometer and chemical shifts are reported in parts per million (ppm) relative to TMS as internal standard.



The mass spectra were run on a Finnigan TSQ-70 spectrometer at 70 eV. The purity of the synthesized compounds was confirmed by thin layer chromatography (TLC) using various solvents of different polarities.

Chemistry: 1,10-Phenanthroline-2,9-dicarbaldehyde (**2**) was prepared from the reaction of 2,9-dimethyl-1,10-phenanthroline (neocuproine) (**1**) with selenium dioxide in 1,4-dioxane as solvent. 1,10-Phenanthroline-2,9-dicarbaldehyde-*bis*-(thiosemi-carbazone) (**3**) was synthesized from 1,10-phenanthroline-2,9-dicarbaldehyde (**2**) and thiosemicarbazide in ethanol under reflux condition.

Preparation of 1,10-phenanthroline-2,9-dicarbaldehyde (2): To a stirring solution of 2,9-dimethyl-1,10-phenanthroline (neocuproine) (1 mmol) was added selenium dioxide (1 mmol) in dioxane containing 4 % water (130 mL) and the reaction mixture was refluxed for 2 h. The precipitate was filtered and recrystallized from acetone giving 1,10-phenanthroline-2,9-dicarbaldehyde as pale yellow crystals.

Yield 70 %, m.p.: 260-266 °C. ¹H NMR (400 MHz, DMSO): [δ = 8.31 (d, 2H_a, J = 8.4 Hz)], [δ = 8.79 (d, 2H_b, J = 8.4 Hz)], [δ = 8.28 (s, 2H_c)], [δ = 10.35 (s, 2H_d)]. IR (KBr, ν_{\max} , cm⁻¹): 1720, 1610, 1570, 1360, 1290.

Preparation of 1,10-phenanthroline-2,9-dicarbaldehyde-*bis*-(thiosemicarbazone) (3): To a stirring solution of 1,10-phenanthroline-2,9-dicarbaldehyde (**2**) (1 mmol) and thiosemicarbazide (2 mmol) in ethanol, was slowly added hydrochloric acid, then the mixture was refluxed for 4 h. The reaction was cooled; the orange precipitated was filtered and recrystallized from ethanol to give compound **3**.

Orange solid, yield 56 %, m.p.: (> 300 °C). ¹H NMR (400 MHz, DMSO): [δ = 8.95 (br s, 2H NH)], [δ = 8.77 (d, 2H_b, J = 8.4 Hz)], [δ = 8.58 (d, 2H_a, J = 8.4 Hz)], [δ = 8.48 (s, 2H_d)], [δ = 8.06 (s, 2H_c)], [δ = 7.46 (br s, 4H NH₂)]. IR (KBr, ν_{\max} , cm⁻¹): 3425, 1604.

MS (m/z, % relative intensity): 382 (M⁺, 10), 330 (12), 304 (12), 281 (75), 252 (15), 227 (12), 181 (17), 91 (44), 71 (31), 57 (59), 43 (100).

Reaction sequence employed for the synthesis of 1,10-phenanthroline-2,9-dicarbaldehyde-*bis*-(thiosemicarbazone) (**3**), is shown in (Scheme-I). Starting material 2,9-dimethyl-

1,10-phenanthroline (neocuproine) (**1**), was converted into 1,10-phenanthroline-2,9-dicarbaldehyde (**2**) in good yield. Compound **3** was obtained by the condensation of compound **2** with thiosemicarbazide in refluxing ethanol (Scheme-I). The structures of synthesized compounds were confirmed by ¹H NMR, IR and mass spectroscopy. Having *bis*-(thiosemicarbazone) on phenanthroline ring, compound **3** should be considered as a useful ligand in coordination chemistry, due to its S and N donor atoms.

Conclusion

In continuation of our research program to find a novel Schiff-base¹⁰, herein we have synthesized and characterized a novel multidentate ligand: 1,10-phenanthroline-2,9-dicarbaldehyde-*bis*-(thiosemicarbazone) (**3**) (Scheme-I). This type of compounds could be considered useful for further investigation in complexation reactions.

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