



NOTE

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

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(Received: 18 May 2011;

Accepted: 22 January 2012)

AJC-11008

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}.

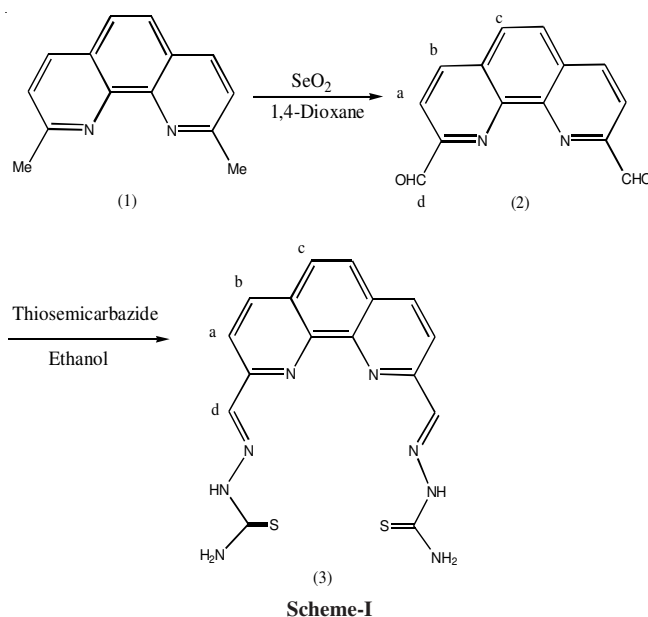
In the area of inorganic chemistry thiosemicarbazide (TSC), ¹NH₂-²NH-C(S)-³NH₂, behaves as a bidentate ligand coordinated through the terminal ¹N and S atoms⁴ and they form highly stable and intensely coloured complexes which are used for spectrophotometric determination of metal ions in different media⁵. 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.

ACKNOWLEDGEMENTS

This work was supported by grants from the research council of Tehran University of Medical Sciences and Iran National Science Foundation (INSF).

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