

Synthesis and Characterization of 9*H*-Carbazole-3-carbaldehyde-4-phenylthiosemicarbazone and 2-Thiophenecarboxaldehyde-4-methylthiosemicarbazone

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Received 20 May 2018 / Accepted 15 June 2018

Abstract: Two Schiff bases 9*H*-carbazole-3-carbaldehyde-4-phenylthiosemicarbazone (CCPTSC) and 2-thiophenecarboxaldehyde-4-methylthiosemicarbazone (TCMTSC) were synthesized. Both the CCPTSC and TCMTSC were characterized by elemental analysis, molar conductivity studies, Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR), and x-ray powder diffraction (XRD). All the spectral studies confirmed that the formation of both CCPTSC and TCMTSC. Thermal stabilities of the both Schiff bases were reported based on thermogravimetric analysis (TGA) studies.

Keywords: Schiff bases, 9*H*-Carbazole-3-carbaldehyde-4-phenylthiosemicarbazone, CCPTSC, 2-Thiophenecarboxaldehyde-4-methylthiosemicarbazone, TCMTSC, Spectral characterization

Introduction

Among various organic chelating agents, thiosemicarbazones occupy a major role by having electron donating nitrogen and sulphur atoms. Thiosemicarbazones are having a great biological activities due to their ability to coordinate to the metal centers in enzymes¹. A number of studies reveal the biological and pharmacological activities of thiosemicarbazones and their metal complexes, such as anti bacterial, anti-viral, anti-malarial and antineoplastic²⁻⁷. Anticancer activities of thiosemicarbazones were reported by various authors over worldwide⁸⁻¹³. Because of having various applications, in recent years a large number of authors reported the synthesis and characterization studies of different thiosemicarbazone ligands¹⁴⁻¹⁸. The importance of thiosemicarbazones both in analytical and biological fields owe to us to synthesize new thiosemicarbazones.

This paper describes synthesis and characterization of two new ligands namely, 9*H*-carbazole-3-carbaldehyde-4-phenylthiosemicarbazone (CCPTSC) and 2-thiophenecarboxaldehyde-4-methylthiosemicarbazone (TCMTSC). These newly synthesized chelating agents were characterized with elemental analysis, Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR), x-ray powder diffraction (XRD). The thermal stabilities of these compounds were established with thermogravimetric analysis studies.

Experimental

All chemicals used in this study were of analytical grade. A Fisher-scientific stirrer with a hot plate was used for stirring and heating the reactants.

Synthesis of 9*H*-carbazole-3-carbaldehyde-4-phenylthiosemicarbazone (CCPTSC)

Methanolic solutions of 1.80 g of 9*H*-carbazole-3-carbaldehyde (M.Wt. 212) in 90 mL and 1.67 g of 4-phenyl-3-thiosemicarbazide (M.Wt. 105.16) in 100 mL were refluxed for approximately 4 h 30 min. in a round bottom flask. The light grey colored product obtained (yield, 82%) was separated by filtration and dried. The product was recrystallized from methanol. The synthesis of CCPTSC is presented in Figure 1.

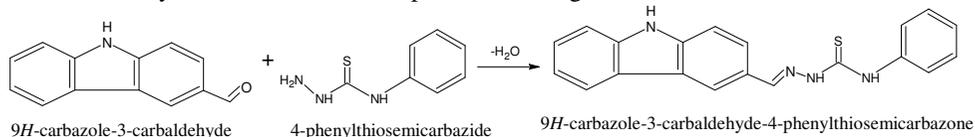


Figure 1. Synthesis of 9*H*-carbazole-3-carbaldehyde-4-phenylthiosemicarbazone (CCPTSC)

Synthesis of 2-thiophenecarboxaldehyde-4-methylthiosemicarbazone (TCMTSC)

TCMTSC was synthesized by refluxing an methanolic solution containing 0.9 mL of 2-thiophenecarboxaldehyde (M.Wt. 112.15, density 1.2 g/mL) and 1.0516 g of 4-methyl-3-thiosemicarbazide (M.Wt. 105.16) for approximately 4 h 30 min. in a round bottom flask. The light yellow colored product obtained (yield, 79%) was separated by filtration and dried. The product was recrystallized from methanol. The synthesis of TCMTSC is presented in Figure 2.

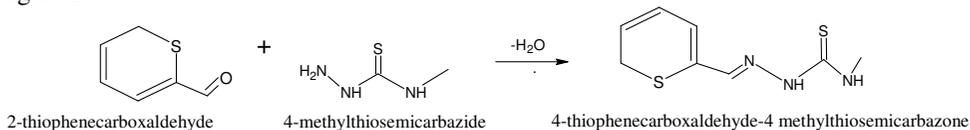


Figure 2. Synthesis of 2-thiophenecarboxaldehyde-4-methylthiosemicarbazone (TCMTSC)

Characterization with elemental analysis, FT-IR, NMR, XRD and TG-DTA

Elemental analysis (N, C, H and S) of both CCPTSC and TCMTSC were recorded on thermo scientific elemental analyzer (Thermo Eager 300 Flash EA1112, USA). Molar conductivity studies were performed with portable molar conductivity meter (MT-115, Manti Lab Solutions, India). The FT-IR spectra were recorded on a Nicolet FT-IR 560 Magna spectrometer. Powder XRD (PAN analytical X'Pert PRO, USA) was carried out using $CuK\alpha$ (0.154056 nm) radiation at 40 kV and 30 mA. The data was collected between 10 and 60° 2 θ with a step size of 0.02°. Thermogravimetric analysis was carried out in the temperature range of 25-800 °C in nitrogen atmosphere and a heating range of 10 °C/min using SDT Q600 V20.9 Build 20 (TA instruments, Waters, USA).

Results and Discussion

CCPTSC and TCMTSC are the newly synthesized and characterized by elemental analysis and various spectral techniques, such as FT-IR, NMR and XRD and its thermal stability was studied by thermogravimetric analysis.

Elemental analysis

Elemental analysis reports of both the chelating agents, CCPTSC and TCMTSC are presented in Figures 3 and 4. The calculated elemental analysis data of CCPTSC ($C_{20}H_{16}N_4S$) is C: 69.74%; H: 4.67%; N: 16.26% and S: 9.31%. This calculated data is well coincide with the experimentally obtained data as C: 67.63%; H: 5.16%; N:15.21% and S: 9.19% to above mentioned formula of CCPTSC. The calculated data for TCMTSC ($C_7H_9N_3S_2$), (C: 42.18%; H: 4.54%; N: 21.08% and S: 32.17%) is in good agreement with the experimentally found data (C: 42.46%; H: 4.45%; N: 21.04% and S: 33.80%) to the above proposed formula for TCMTSC.

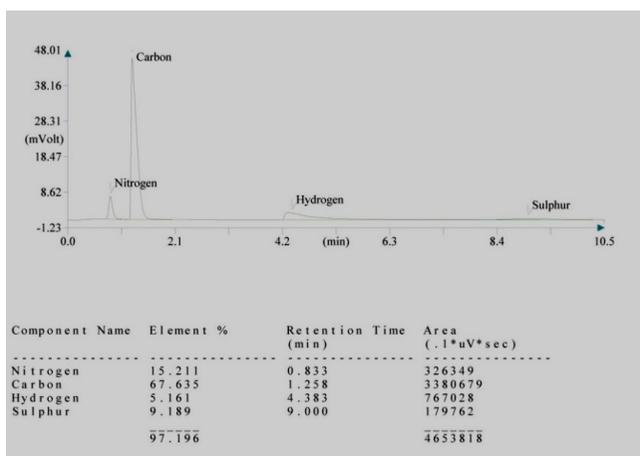


Figure 3. Elemental analysis report of CCPTSC

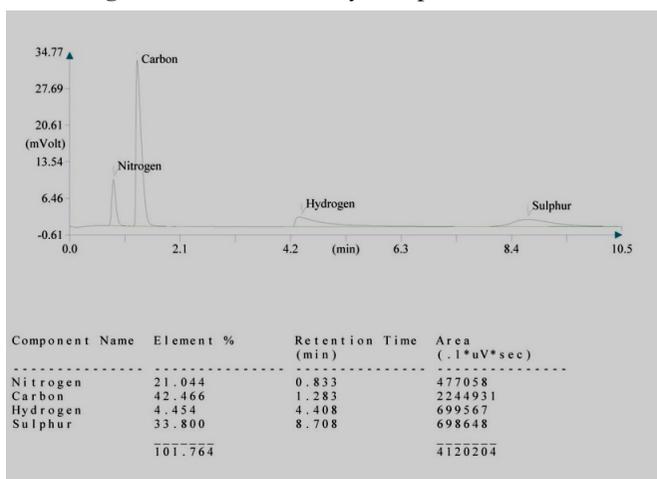


Figure 4. Elemental analysis report of TCMTSC

FT-IR analysis

FT-IR spectrum of CCPTSC is presented in Figure 5. The spectral data of CCPTSC is as follows: C=N peak at 1635 cm^{-1} , C=S peak at 1222 cm^{-1} and -NH peak at 3300 cm^{-1} . This data confirms the formation of the chelating agent, CCPTSC. Figure 6 represents the FTIR spectrum of TCMTSC. FT-IR spectral data of TCMTSC is as follows, C=N peak appears at 1624 cm^{-1} and -NH peak at 3312 cm^{-1} . This data confirms the formation of the chelating agent, TCMTSC.

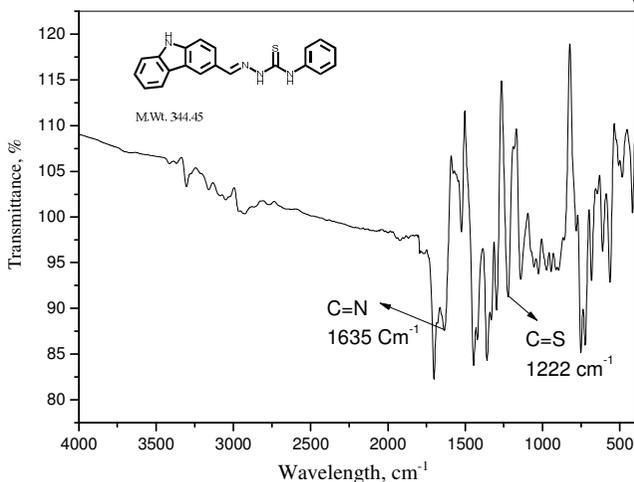


Figure 5. FT-IR spectrum of CCPTSC

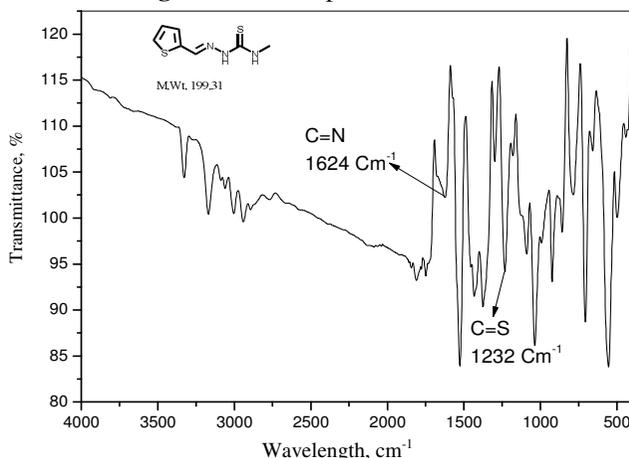


Figure 6. FT-IR spectrum of TCMTSC

^1H NMR spectral analysis

^1H NMR data (DMSO/TMS) of CCPTSC is as follows: ^1H NMR (300 MHz, DMSO- d_6): δ =9.91 (s, 1H), 9.12 (s, 1H), 8.47 (s, 1H), 8.18 (d, 2H), 7.65 (d, 2H), 7.57-7.43 (m, 4H), 7.29 (m, 2H), 7.09 (m, 2H), 4.8 (broad, 1H). This ^1H NMR data confirms the formation of CCPTSC. The ^1H NMR spectrum of CCPTSC is presented in Figure 7. ^1H NMR data (DMSO/TMS) of TCMTSC is as follows: ^1H NMR (300 MHz, DMSO- d_6): δ =11.44 (s, 1H), 8.24 (s, 1H), 8.13 (q, 1H), 7.64 (d, 2H), 7.43 (d, 2H), 7.10 (t, 3H), 3.00 (d, 3H). This ^1H NMR data confirms the formation of TCMTSC. ^1H NMR spectrum of TCMTSC is presented in Figure 8.

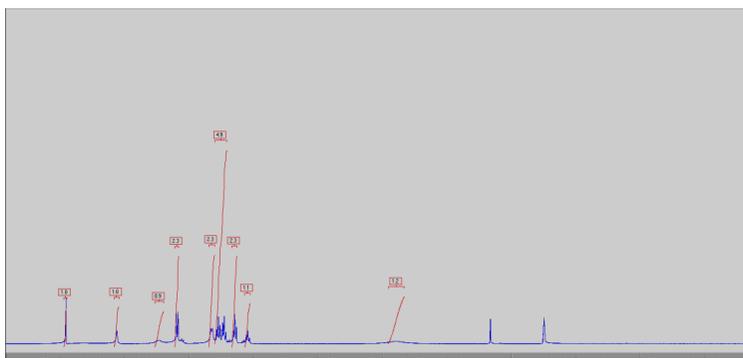


Figure 7. ^1H NMR spectrum of CCPTSC

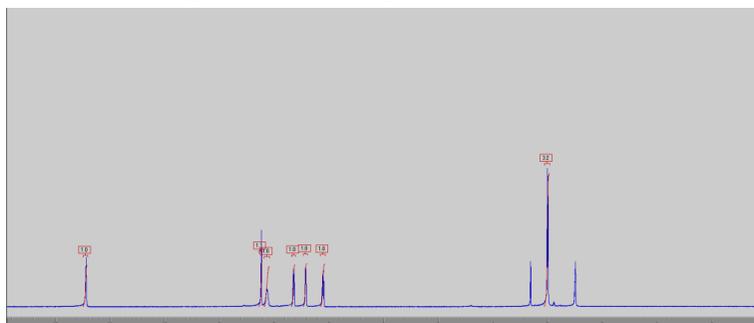


Figure 8. ^1H NMR spectrum of TCMTSC

XRD analysis

XRD was carried out to identify the crystalline nature of the newly synthesized chelating agents. Figures 9 and 10 show XRD patterns of CCPTSC and TCMTSC respectively. Both the chelating agents were polycrystalline in nature. The dominant XRD peak at $20.50^\circ 2\theta$ was observed for CCPTSC, while the peak for TCMTSC was observed at $29.95^\circ 2\theta$.

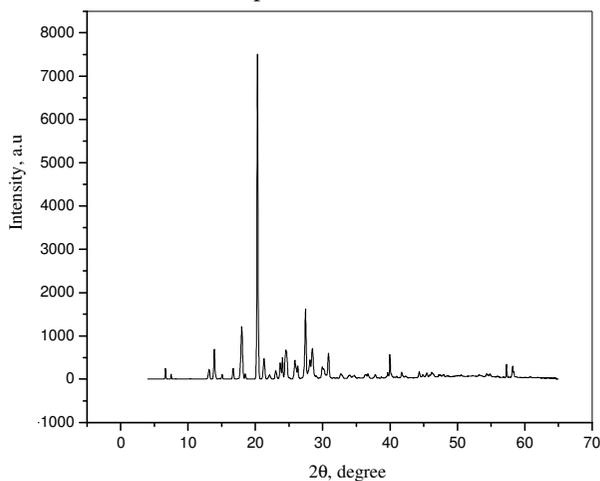


Figure 9. XRD spectrum of CCPTSC

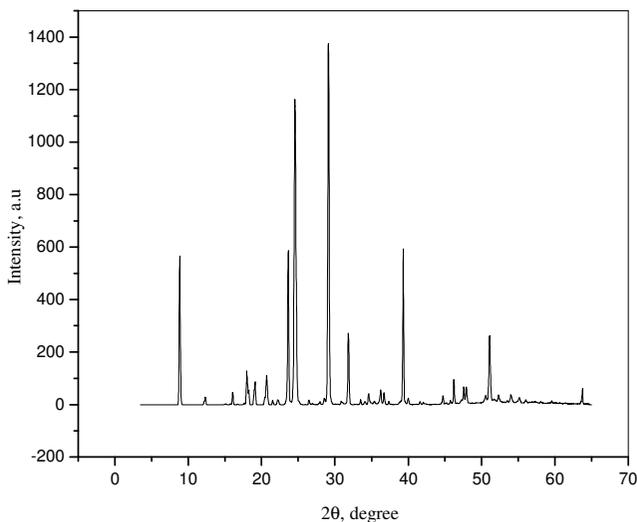


Figure 10. XRD spectrum of TCMTSC

Thermogravimetric analysis

The thermogravimetric graphs of CCPTSC and TCMTSC are presented in Figures 11 and 12 respectively. The thermogravimetric diagram of CCPTSC shows that the chelating agent starts melting at 88 °C, the decomposition occurs at 238 °C with a weight loss of 55% and almost 95% weight loss observed at 800 °C. The thermogravimetric diagram of TCMTSC indicates that the compound starts melting at 170 °C and the decomposition occurs at 300 °C with a weight loss 86% and more than 98% weight loss observed at 800 °C. Based on melting temperatures, it is observed that the TCMTSC is having more thermal stability than CCPTSC.

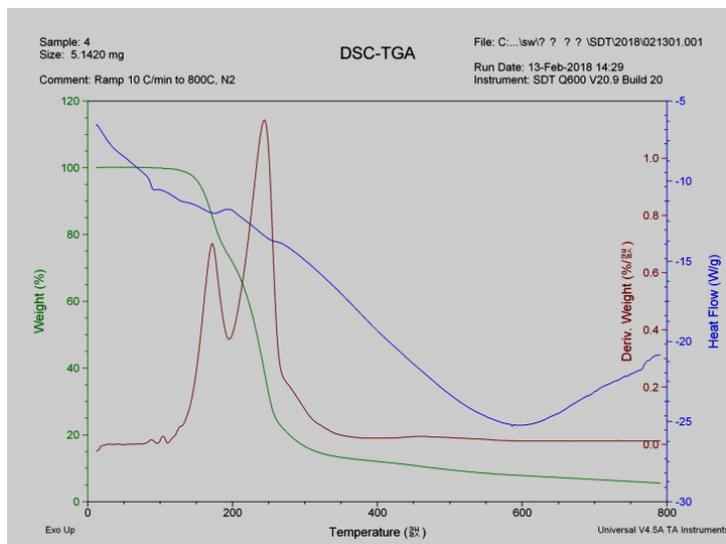


Figure 11. TGA spectrum of CCPTSC

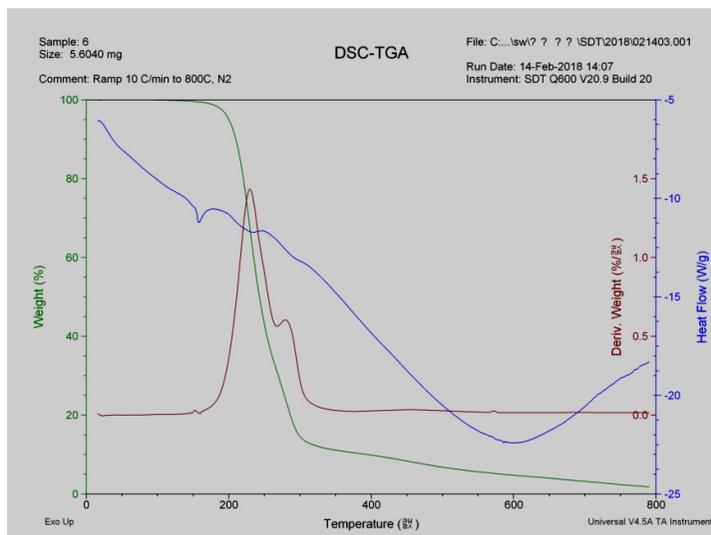


Figure 12. TGA spectrum of TCMTSC

Conclusion

Based on the present study, it confirms that the synthesis of two new organic chelating agents namely, H-carbazole-3-carbaldehyde-4-phenylthiosemicarbazone (CCPTSC) and 2-thiophenecarboxaldehyde-4-methylthiosemicarbazone(TCMTSC). The formation of these organic chelating agents was also confirmed by the elemental analysis studies and various spectral techniques, such as FT-IR, ^1H NMR and XRD. The thermogravimetric analysis reveals that the two compounds lost more than 95% weight at 800 °C. These organic chelating agents can be used for the complexation with various transitional metal ions. The biological activities of both the chelating agents and their metal complexes will be evaluated in our future studies.

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