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RESEARCH ARTICLE

Synthesis and Characterization of 10-Hexyl-10*H*-phenothiazine-3-carbaldehyde-4-phenylthiosemicarbazone and 4-Methylbenzaldehyde-4-methylthiosemicarbazone

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Abstract: Two Schiff bases 10-hexyl-10*H*-phenothiazine-3-carbaldehyde-4-phenylthiosemicarbazone (HPCPTSC) and 4-methylbenzaldehyde-4-methylthiosemicarbazone (MBMTSC) were synthesized. Both the HPCPTSC and MBMTSC 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 HPCPTSC and MBMTSC. Thermal stabilities of the both Schiff bases were reported based on thermogravimetric analysis (TGA) studies

Keywords: Schiff bases, 10-Hexyl-10*H*-phenothiazine-3-carbaldehyde-4-penylthiosemicarbazone, HPCPTSC, 4-Methylbenzaldehyde-4-methylthiosemicarbazone, MBMTSC, Spectral characterization

Introduction

Organic chelating agents had various applications in different fields, such as medical[1-3], pharmaceutical[4-9] and biological[10-12]. Due to the presence of electron donating groups, such as sulpur and nitrogen atoms they can bind with metal ions in enzymes. Among these chelating agents, thiosemicarbazones are an important class of compounds with a high potential biological activities not limited to anti-bacterial, viral, tripanosomal, malarial and cancer[13-15]. These thiosemicarbazones are an important group of ligands can bind with both the hard and soft donor atoms will result the great coordination behavior[16]. Because of the great importance of thiosemicarbazones in various fields, we synthesized two new chelating agents.

This paper describes the synthesis of two new Schiff bases, 10-hexyl-10*H*-phenothiazine-3-carbaldehyde-4-phenylthiosemicarbazone (HPCPTSC) and 4-methyl-benzaldehyde-4-methylthiosemicarbazone (MBMTSC). These newly synthesized chelating agents were characterized with elemental analysis, Fourier transform infrared spectroscopy

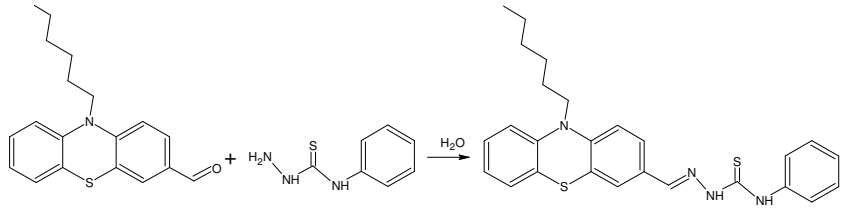
(FT-IR), nuclear magnetic resonance spectroscopy (NMR), x-ray powder diffraction (XRD). Thermal stabilities of these compounds were established with thermogravimetric analysis studies.

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 10-hexyl-10H-phenothiazine-3-carbaldehyde-4-penylthiosemicarbazone (HPCPTSC)

Methanolic solutions of 1.15 g of 10-hexyl-10*H*-phenothiazine-3-carbaldehyde (M.Wt. 212) in 75 mL and 0.83 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 yellow colored product obtained (yield, 82%) was separated by filtration and dried. The product was recrystalized from methanol. The synthesis of HPCPTSC is presented in Figure 1.

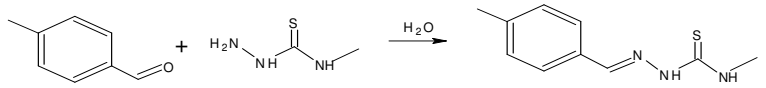


10-Hexyl-10*H*-phenothiazine-3-carbaldehyde 4-Phenylthiosemicarbazide 10-Hexyl-10*H*-phenothiazine-3-carbaldehyde-4-penylthiosemicarbazone

Figure 1. Synthesis of 10-hexyl-10*H*-phenothiazine-3-carbaldehyde-4-penylthiosemicarbazone

Synthesis of 4-methylbenzaldehyde-4-methylthiosemicarbazone (MBMTSC):

MBMTSC was synthesized by refluxing a methanolic solution containing 1.1 mL of 4-methylbenzaldehyde (M.Wt. 120.15 g, density 1.019 g/mL) and 1.0516 g of 4-methyl-3-thiosemicarbazide (M.Wt. 105.16 g) for approximately 4 h 30 min. in a round bottom flask. The white colored product obtained (yield, 80%) was separated by filtration and dried. The product was recrystallized from methanol. The synthesis of MBMTSC is presented in Figure 2.



4-Methylbenzaldehyde 4-Methylthiosemicarbazide 4-Methylbenzaldehyde-4-methylthiosemicarbazone

Figure 2. Synthesis of 4-methylbenzaldehyde-4-methylthiosemicarbazone (MBMTSC)

Characterization with Elemental Analysis, molar conductivity, FT-IR, NMR, XRD and TG-DTA

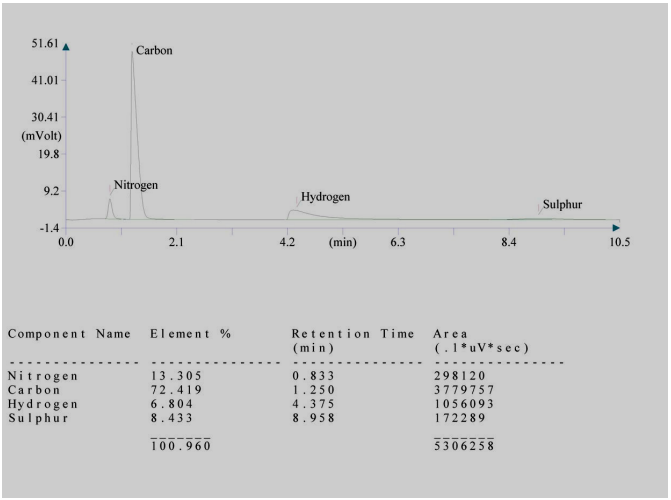
Elemental analysis (N, C, H and S) of both CCPTSC and TCMTSC were recorded on Thermo Scientific elemental analyzer (Thermo Eager 300 Flash EA1112, USA). Molar conductivity studies were performed with portable molar conductivity meter (MT-115, Manti Lab Solutions, India). The FT-IR spectra were recorded on a Nicolet FT-IR 560 Magna spectrometer. Powder XRD (PAN analytical X'Pert PRO, USA) was carried out using CuK_α (0.154056 nm) radiation at 40 kV and 30 mA. The data was collected between 10 and 60°2θ 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

HPCPTSC and MBMTSC 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.

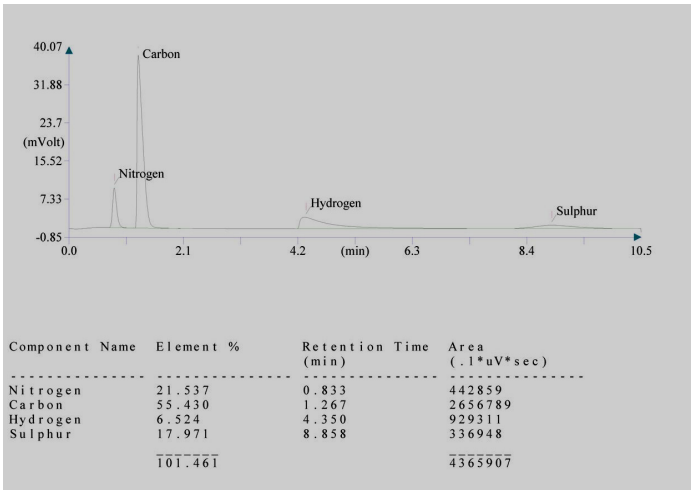
Elemental analysis

Elemental analysis reports of both the chelating agents, HPCPTSC and MBMTSC are presented in Figures 3 and 4. The calculated elemental analysis data of HPCPTSC ($C_{26}H_{28}N_4S_2$) is C: 67.79%; H: 6.12%; N: 12.16% and S: 13.92%. This calculated data is well coincide with the experimentally obtained data as C: 72.41%; H: 6.80%; N: 13.30% and S: 8.43% to above mentioned formula of HPCPTSC. The calculated data for MBMTSC ($C_{10}H_{13}N_3S$), (C: 57.94%; H: 6.31%; N: 20.27% and S: 15.46%) is in good agreement with the experimentally found data (C: 55.43; H: 6.52%; N: 21.53% and S: 17.97%) to the above proposed formula for MBMTSC.



Component Name	Element %	Retention Time (min)	Area (.1*uV*sec)
Nitrogen	13.305	0.833	298120
Carbon	72.419	1.250	3779757
Hydrogen	6.804	4.375	1056093
Sulphur	8.433	8.958	172289
	100.960		5306258

Figure 3. Elemental analysis report of HPCPTSC



Component Name	Element %	Retention Time (min)	Area (.1*uV*sec)
Nitrogen	21.537	0.833	442859
Carbon	55.430	1.267	2656789
Hydrogen	6.524	4.350	929311
Sulphur	17.971	8.858	336948
	101.461		4365907

Figure 4. Elemental analysis report of MBMTSC

FT-IR analysis

FT-IR spectrum of HPCPTSC is presented in Figure 5. The spectral data of HPCPTSC is as follows: C=N peak at 1625 cm^{-1}, C=S peak at 1236 cm^{-1} and -NH peak at 3310 cm^{-1}. This data confirms the formation of the chelating agent, HPCPTSC. Figure 6 represents the FTIR spectrum of MBMTSC. FT-IR spectral data of MBMTSC is as follows, C=N peak at 1629 cm^{-1}, C=S peak at 1236 cm^{-1} and -NH peak at 3320 cm^{-1}. This data confirms the formation of the chelating agent, MBMTSC.

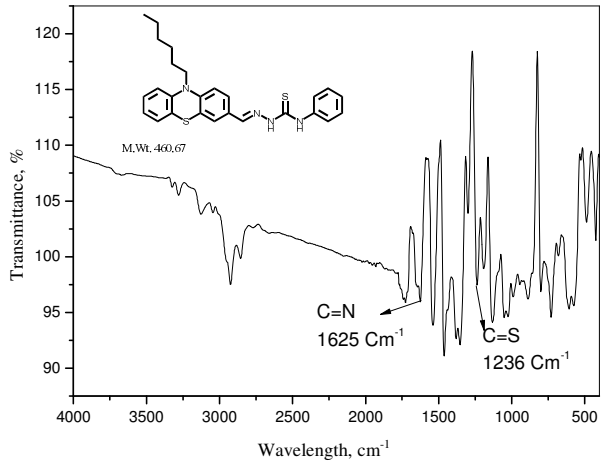


Figure 5. FT-IR spectrum of HPCPTSC

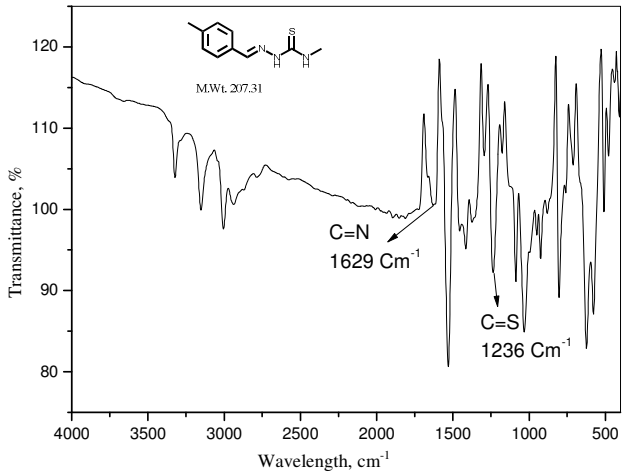


Figure 6. FT-IR spectrum of MBMTSC

^{1}H NMR spectral analysis

^{1}H NMR data (DMSO/TMS) of HPCPTSC is as follows: ^{1}H NMR (300 MHz, DMSO-d6): d=11.80 (s, 1H), 10.08 (s, 1H), 8.63 (s, 1H), 8.35 (s, 1H), 8.22 (d, 2H), 8.07(d, 1H), 7.63 (m, 5H), 7.52-7.36 (m, 2H), 7.2 (m, 2H), 4.41 (t, 3H), 1.76 (q, 2H), 1.24 (m, 6H), 0.79 (t, 3H). This ^{1}H NMR data confirms the formation of HPCPTSC. ^{1}H NMR spectrum of HPCPTSC is presented in Figure 7. ^{1}H NMR data (DMSO/TMS) of MBMTSC is as follows: ^{1}H NMR

(300 MHz, DMSO-d6): d=11.40 (s, 1H), 8.45 (d, 1H), 8.01 (s, 1H), 7.68 (d, 2H), 7.23 (d, 2H), 3.01 (d, 3H), 2.32 (s, 3H). This ^{1}H NMR data confirms the formation of MBMTSC. ^{1}H NMR spectrum of MBMTSC is presented in Figure 8.

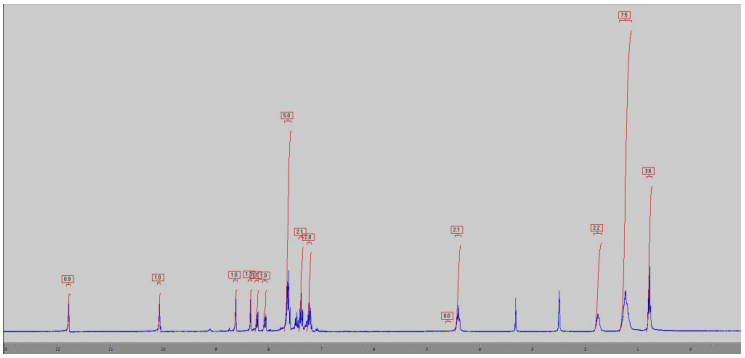


Figure 7. ^{1}H NMR spectrum of HPCPTSC

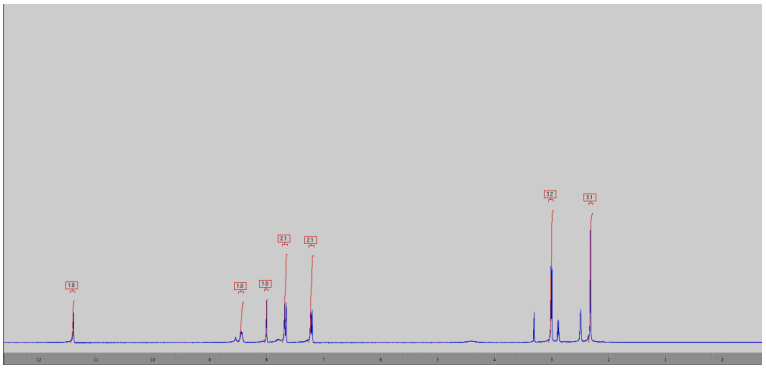


Figure 8. ^{1}H NMR spectrum of MBMTSC

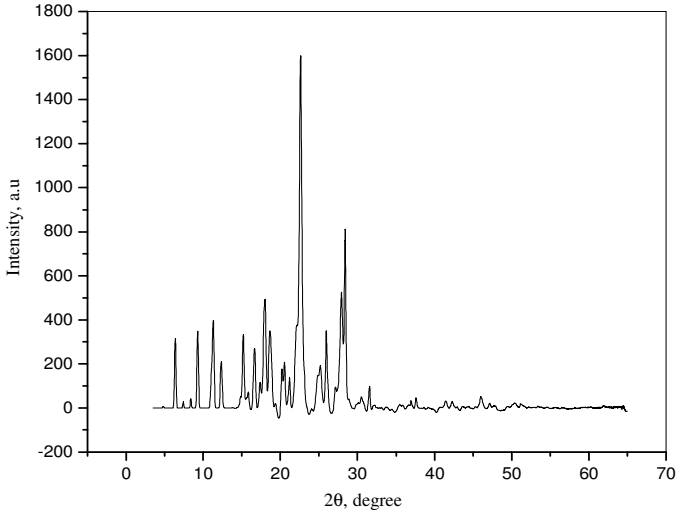


Figure 9. XRD spectrum of HPCPTSC

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 HPCPTSC and MBMTSC, respectively. Both the chelating agents were polycrystalline in nature. The dominant XRD peak at 22.50° 2θ was observed for CCPTSC, while the peak for MBMTSC was observed at 22.75° 2θ.

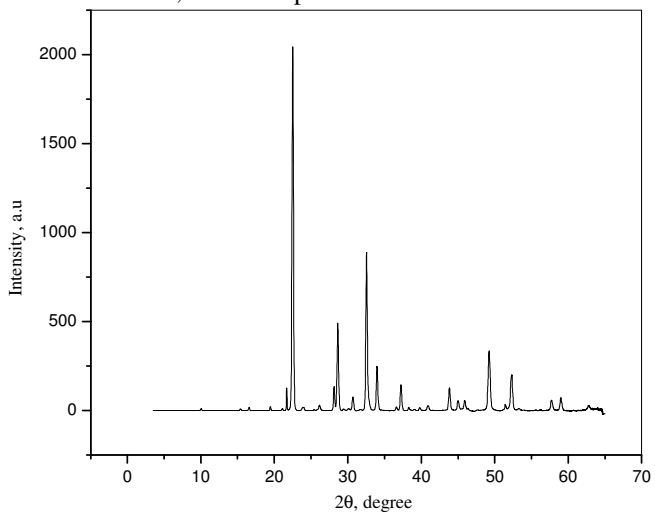


Figure 10. XRD spectrum of MBMTSC

Thermogravimetric analysis

The thermogravimetric diagrams of both HPCPTSC and MBMTSC are presented in Figures 11 and 12, respectively. From the thermogravimetric diagram of HPCPTSC, it is observed that the compound starts melting at 94 °C and the decomposition occurs at 250 °C with a weight loss of 40% and more than 98.5% weight loss observed at 800 °C. From the thermogravimetric diagram of MBMTSC indicates that the melting of the compound starts at 106 °C and the decomposition occurs at 300 °C with a weight loss of 88% and nearly 100% weight loss occurred at 800 °C. Based on the thermogravimetric studies, it is concluded that HPCPTSC is more stable than MBMTSC.

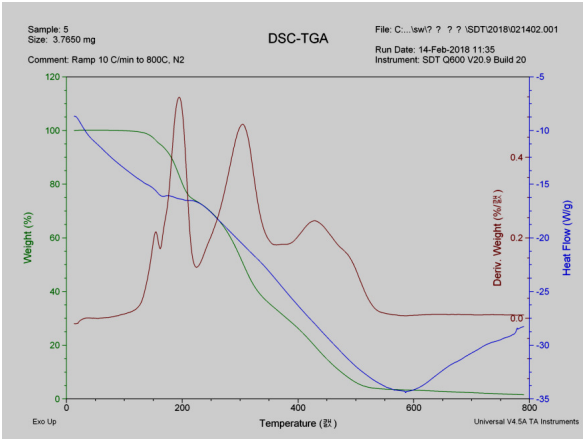


Figure 11. TGA spectrum of HPCPTSC

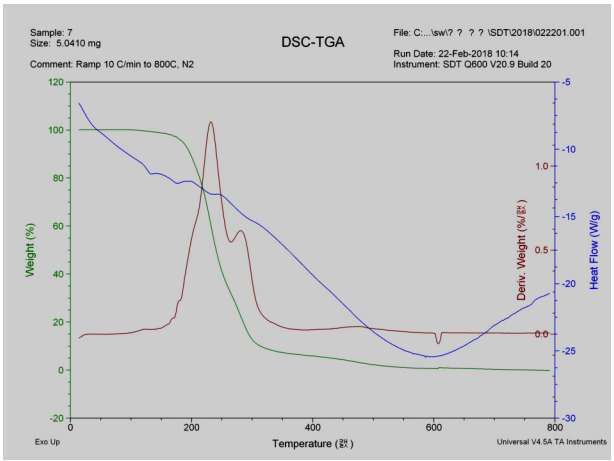


Figure 12. TGA spectrum of MBMTSC

Conclusion

The present study concludes that the synthesis of two new organic chelating agents namely, 10-hexyl-10*H*-phenothiazine-3-carbaldehyde-4-phenylthiosemicarbazone (HPCPTSC) and 4-methylbenzaldehyde-4-methylthiosemicarbazone (MBMTSC). The formation of these organic chelating agents was also confirmed by the elemental analysis studies and various spectral techniques, such as FT-IR, ^{1}H NMR and XRD. The thermogravimetric analysis reveals that HPCPTSC is more stable than MBMTSC. 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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