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VPS-41

# SYNTHESIS, CHARACTERIZATION OF Pt(II) COMPLEX OF CAMPHOR 4-PHENYL THIOSEMICARBAZONE

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### Abstract

The complex of Pt(II) with campbor 4-phenyl thiosemicarbazone was synthesized and characterized by means of MS, IR, <sup>1</sup>H-NMR and UV-VIS spectroscopies. Results showed that, the molecular formula of complex of Pt(II) = a camphor 4-phenyl thiosemicarbazone is  $[Pt(C_{17}H_{22}N_3S)_2]$ . The Pt(II) complex is four coordinate and square planar geometry.

Keywords. camphor 4-phenyl thiosemicarbazone, complex of Pt(II).

# 1. INTRODUCTION

Platinum-based anticancer drugs are the mainstay of chemotherapy regimens in clinic. Nevertheless, the efficacy of platinum drugs is badly affected by systemic toxicities and drug resistance, and the pharmacokinetics of most platinum drugs is largely unknown [1, 2, 3]. In recent years, platinum complexes with bioactive molecules, natural compounds, targeting groups or nonmaterial's has been interested by chemical and biomedical researchers [4, 5, 6]. The motivation comes from some of the following demands: improve the selectivity or minimize the systemic toxicity of the drugs, enhance the cellular accumulation of the drugs, overcome the tumor resistance to the drugs, visualize the drug molecules in vitro or in vivo, achieve a synergistic anticancer effect between different therapeutic modalities, or to add extra functionality to the drugs [5, 6]. The development of drug delivery systems in the last several decades has provided a variety of methods including the synthesis new Pt(II), Pt(IV) complexes, the incorporation of drugs into liposome's, lipid emulsions, and polymeric micelles to reduce side effects, to increase their solubility, and to prolong circulation time as well [6]. Camphor has bioactivity, it has been used in traditional medicine from time immemorial. The coordination of camphor and platinum could create new compounds with high bioactivity. In this paper, we present the new results of Pt(II) complex with camphor 4-phenyl thiosemicarbazone.

# 2. CHEMICALS AND METHOD

## 2.1. Chemicals

Camphor, 4-phenyl thiosemicarbazide, acert acid and ethanol were purchased from Merca K<sub>2</sub>[PtCl<sub>4</sub>] was purchased from Sigma - Aldrich.

# 2.2. Method

# 2.2.1. Synthesis of camphor 4-phere thiosemicarbazone (H4thiocam)

The H4thiocam was prepared from 4-phere thiosemicarbazide and camphor (1:1 molar rational The H4thiocam was prepared from 4-phere thiosemicarbazide and camphor (1:1 molar rational The mixture of reactants was dissolved in the ethanol and anhydrous acetic acid was added until pH reached 3-4. This mixture was stirred and refut at 70 °C for 6 h. After cooling to room temperature crystalline product was isolated and washed the water, ethanol-water, and dried over P-H4thiocam was obtained as a white powder.

# 2.2.2. Synthesis of Pt(II) Complex (Pt-4thiocam)

To synthesize Pt-4thiocam, a solution of K<sub>2</sub>[PtCl<sub>4</sub>] (0.415 g, 0.001 mole) in 50 mL water added to a solution of camphor 4-pherethiosemicarbazone (0.602 g, 0.002 mole) in 100 mL ethanol at 30 °C under stirring for 1 h.The reaction mixture was kept at ~10 °C for 24 h. Afterware the precipitate was filtered and washed severatimes with water, ethanol, and dried over P<sub>2</sub>O<sub>5</sub>. The Pt-4thiocam was obtained as a dark yellow powder

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#### 2.3. Structure determination

Mass spectroscopy with electro spray onization technique (ESI-MS) was used in order to confirm the formula of H4thiocam and Pt-4thiocam Agilent 1100 LC/MSD Trap). IR spectra were eccorded with a FTIR Shimadzu spectrophotometer using KBr discs in the frequency range of 4000-400 cm<sup>-1</sup>. <sup>1</sup>H-NMR spectra were obtained with a Bruker 500 MHz spectrometer and the chemical shifts tare given in units of  $\delta$  relative to TMS as an internal sundard using DMSO-d6 as the solvent.

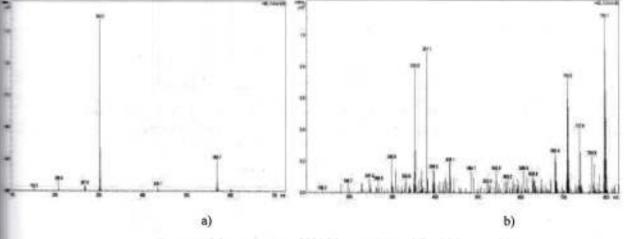
## RESULTS AND DISCUSSION

ESI/MS data in Table 1. As seen in the MS spectra (Figure 1(a,b)), the appearance of a cluster of peaks with m/z = 302, 303, 304 of H4thiocam (Fig. 1(a)) and a cluster of peaks with m/z = 795, 796, 797 of Pt-4thiocam (Fig. 1(b)) were consistent with the molecular formula of ligand  $C_{17}H_{23}N_{1}S$  and the complex Pt( $C_{17}H_{22}N_{3}S$ )<sub>2</sub> calculated from different isotopes.

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# Table 1. MS data and compound's molecular formula

Sample	m/z,[M] <sup>+</sup> / [M+H] <sup>+</sup>	М	Molecular formula	
H4thiocam	302	301	C17H23N3S	
Pt-4thiocam	795	795	Pt(C17H22N3S)2	





The <sup>1</sup>H-NMR spectrum of H4thiocam (Figure a)) exhibited a singlet at 10.16 ppm attributed to MI-hydrazine proton. The presence of NH signal indicated the presence of H4thiocam in the thione im. The proton signal on the NH-amide appeared 9.64 ppm. The signals in range 7.15 to 7.59 ppm are assigned to 5H of benzyl ring. Triplet signals 0.73 ppm to 1.03 ppm were assigned to 9H of CH<sub>3</sub> groups and signals in range 1.19 to 2.63 ppm are assigned to protons of CH and CH<sub>2</sub>. The sence of H signal of NH-hydrazine (NHC=S pup) from Pt-4thiocam complex's spectrum Figure 2(b)) confirmed the deprotonation of the legand due to coordination with Pt(II) via S and N. The signals of other protons appeared in similar ange in ligand's spectrum The NMR results were mistent with IR results.

The IR spectrum of H4thiocam (Fig. 3a) indicated the coordination of the azomethine cowed absorption bands at 3360 and 3278 cm<sup>4</sup>ue nitrogen. This result was confirmed by the presence Please purchase PDF Split-Merge on www.verypdf.com to remove this watermark.

to stretching frequencies for NH-amide and NHhydrazine. The band due to the -SH group was not observed in 2500-2600 cm<sup>-1</sup> and the presence of band at 760 cm<sup>-1</sup> due to v(C=S) suggested the existence of thiosemicarbazone in the thione form. The absorptions band for - CN appeared at 1593 cm1. The IR spectrum of Pt-4 thiocam (Fig. 3b) showed absorption band at 3383 cm<sup>-1</sup> due to stretching frequencies for NH-amide, while the absorption for NH at region 3000-3200 cm<sup>-1</sup> was absent. The v(C=S) band at 760 cm<sup>-1</sup> in the spectrum of the ligand shifted to 751 cm<sup>-1</sup> in the spectrum of the complex, indicated that the existence of ligand is in the thiol form and deprotonation on complexation and that Pt(II) coordinated with the thiolate sulfur. The v(C=N) band of the thiosemicarbazone at 1593 cm<sup>-1</sup> shifted to 1549 cm<sup>-1</sup> in the spectrum of the complex, indicated the coordination of the azomethine

of new bands at 601 and 501 cm<sup>-1</sup> due to  $v_{(Pt-N)}$  and  $v_{(Pt-S)}$ . These spectra suggested that after deprotonation the ligand coordinated with the  $Pt(\rm II)$ 

via S and N. Selected IR bands for the light (H4thiocam) and complex (Pt-4thiocam) are g = in Table 2.

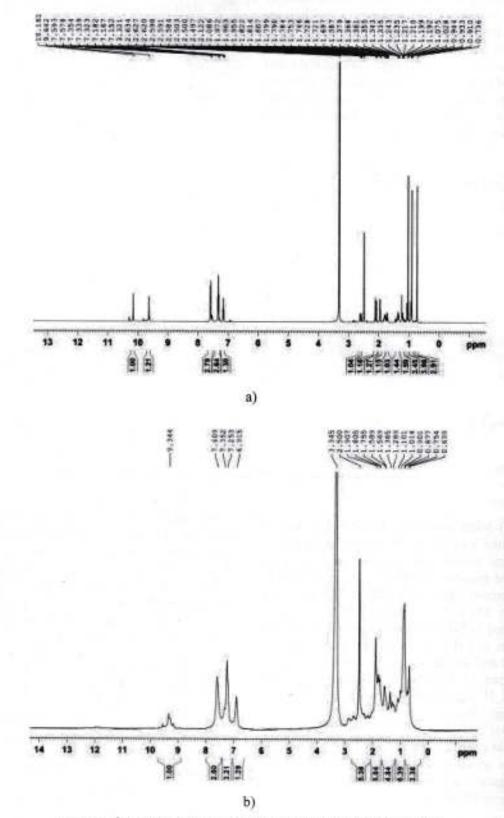


Figure 2. <sup>1</sup>H-NMR spectra of H4thiocam (a) and Pt-4thiocam (b) Please purchase PDF Split-Merge on www.verypdf.com to remove this watermark.

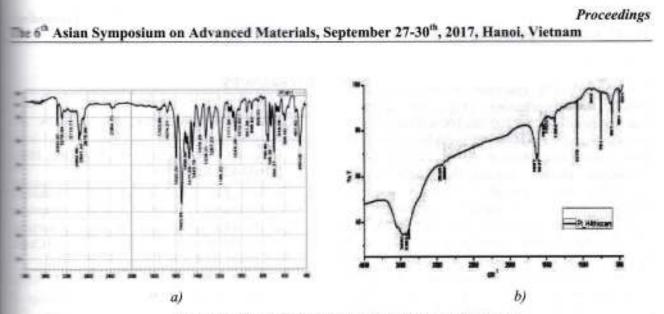
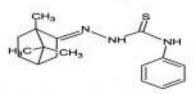


Figure 3. IR spectra of H4thiocam (a) and Pt-4thiocam (b)

Table 2. Selected IR bands of th	e H4thiocam and Pt-4thiocam
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v, cm <sup>-1</sup>	v <sub>NH</sub>	$v_{CN} + v_{Ar}$	V <sub>NN</sub>	v <sub>CS</sub>	$\nu_{\text{Pt-X}}(X{=}S,N)$
54thiocam	3360, 3278	1593, 1543	1049	760	-
thiocam	3383	1549, 1503	1078	751	601, 501

Based on the above analysis, reasonable structures of H4thiocam ligand and Pt-4thiocam complex are incided in Fig. 4.



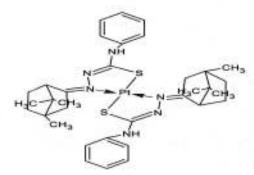
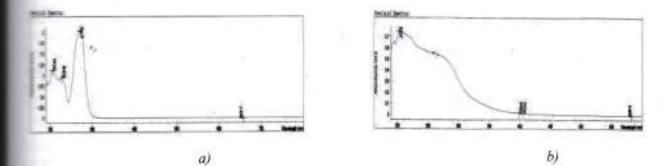


Figure 4. Structures of the H4thiocam and Pt-4thiocam



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The UV-VIS spectrum of the camphor 4phenyl thiosemcarbazone (Fig. 5a) appeared absorbance only in the 200 nm-300 nm range of the internal ligand transfer, on the complex's spectrum, these absorbencies have a red shift to the longer wavelength region, showing the change of the ligand from free to complex. The spectrum of the Pt(II) complex (Fig. 5b), appeared two absorbencies of the internal ligand transfer and charge transfer at 200 nm - 400 nm. The absorbance with wide, weak intensity in the 400-450nm range is characteristic of the d-d transfer band, corresponding to the square planar geometry. The UV-VIS spectrum of Pt(II) complex with 4-phenyl thiosemicarbazone camphor is consistent with the results of UV-VIS spectra of Pt(II) complexes which were studied by some authors [3, 4].

# 4. CONCLUSION

In conclusion, the complex of camphor 4phenyl thiosemicarbazone with Pt(II) was successfully synthesized from K2[PtCl4] and camphor 4-phenyl thiosemicarbazone in ethanolwater solvent. The analysis data from MS, IR, 'H-NMR and UV-VIS spectra showed that the molecular formula of complex of Pt(II) with camphor 4-phenyl thiosemicarbazone is [Pt(C17H22N3S)2]. The Pt(II) complex is four coordinate and square planar geometry.

#### ACKNOWLEDGMENTS

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