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Chemical characterization using the infrared spectra to remove sulfur element from thiourea compound as a one of the organic compounds present in crude oil using a modern method: Metal ions plays the role of catalyst

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Abstract: Manganese, zinc and cadmium(II) thiocyanate, $M(SCN)_2 \cdot xH_2O$, is obtained by a new synthetic method involving the reaction of aqueous solutions of $MnCl_2$, $Zn(NO_3)_2 \cdot 6H_2O$ and $CdCl_2$ with thiourea at $\sim 90^\circ C$. The infrared spectrum of the formed product clearly indicates the absence of bands due to thiourea and shows the characteristic bands of thiocyanate ion. A general mechanism describing the formation of metal thiocyanate, $M(SCN)_2 \cdot xH_2O$, is suggested.

Keywords: thiocyanate SCN^- , infrared spectra, transition metals, thiourea.

I. INTRODUCTION

Different metal complexes of thiourea rich ligand exhibit an interesting efficiency toward biological activity including anticancer [1], antimicrobial [1-3], antibacterial [4], antifungal [5], antimalarial [6] and antituberculosis [7]. There have been many researches of benzoyl-substituted thioureas and related ligands coordinated to metals where the ligand usually coordinated through S and O, giving a six membered ring system [3-5]. They are able to coordinate to arrange metal centres as neutral ligands or as anionic ligands [8,9]. As some reports demonstrated that the antibacterial activity of some compounds becomes enhanced when they are complexed with copper [4, 10]. Some investigations on cobalt(II) substituted complexes show that Co(II) has a pronounced tendency to form tetrahedral complexes with general formula CoL_2X_2 (X= nitrate or acetate; L= thiourea derivatives) [11]. This paper deals with the formation of the new compounds by the interaction of thiourea with some transition metals at high temperatures, and this important point has not been noted in previous research in research journals. The research aims also to use thiourea as a model for some organic compounds containing the element sulfur and non-desirable quality in crude oil and how to get rid of it by using the transition elements as catalysts.

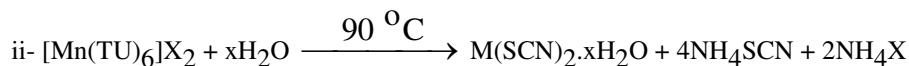
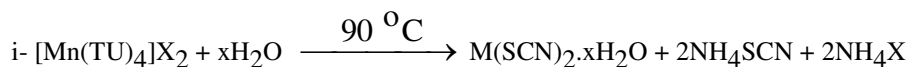
II. EXPERIMENTAL

Reagent grade chemicals were used throughout. $M(SCN)_2 \cdot xH_2O$ was prepared by mixing equal aqueous solutions (50 mL) of 0.01 mol of manganese(II) chloride, $Zn(NO_3)_2 \cdot 6H_2O$ or $CdCl_2$ salts with (50 mL) of 0.1 mol thiourea. The mixtures were heated to ca. $90^\circ C$ for 8-10 h in a hotplate. The precipitated buff, yellowish white and yellow of Mn(II),

Zn(II) and Cd(II) thiocyanate compounds were filtered, washed several times with hot water, dried at 90 °C in an oven for 3 h. The yields were in ratio 40-50 %. Manganese, cadmium and zinc elements were determined gravimetrically as manganese dioxide, MnO₂, cadmium oxide, CdO and zinc oxide, ZnO, respectively. The IR spectra of thiourea and all final products were recorded in Bruker FT-IR Spectrophotometer.

III.RESULTS AND DISCUSSION

The reaction of aqueous solutions of thiourea and MnCl₂, Zn(NO₃)₂.6H₂O or CdCl₂ salts at ca. ~ 90 °C produces a buff, yellowish white and yellow solid products, respectively. The infrared spectra of the solid products are shown in Fig. 1 and its band assignments are given in Table 1. The infrared spectra of the obtained product shows no bands due to coordinated thiourea, but instead, a group of bands characteristic for ionic thiocyanate [12], SCN⁻, appeared. Based on this fact, along with comparing the outputs products in this paper with that the infrared spectra of commercially obtained Cu(SCN)₂ and Ba(SCN)₂ (Fig. 2) [13] are the same as that of the reaction product, the product obtained were identified as M(SCN)₂.xH₂O, (where M= Mn, Zn, Cd(II)). The IR assignments agree quite well with those generally known for the ionic thiocyanate, SCN⁻. When a comparison between important study for Nour and Rady [14] that reported the synthesis of the isocyanate salt, AgNCO, by the new method of reacting aqueous solutions of silver nitrate and urea at Ca. 80 °C. It can be said that one of the possible ways to get the thiocyanate salts and isocyanates in a simple manner is the interaction between urea or thiourea with some salts of the transition metals and we can not generalize to all of the transition metal salts and the resulting climate is also influenced by the ion associated with the transitional element, too. We could say that this research is beginning to study the products of the reaction between thiourea compound and the rest of the transition metals and their different anions like chloride, sulfate, nitrate and acetate and so. The role of Mn(II), Zn(II) or Cd(II) ions in decomposing the coordinated thiourea at high temperature may be understood as follows. At room temperature, manganese(II), zinc(II) or cadmium(II) ions react with thiourea to form the suggested complexes [M(TU)₆]X₂ and [M(TU)₄]X₂. (M= Mn(II), Zn(II) or Cd(II); TU= thiourea). At high temperature, the following reaction may take place:



(where: M= Mn, Zn or Cd(II); X= Cl⁻ or NO₃⁻)

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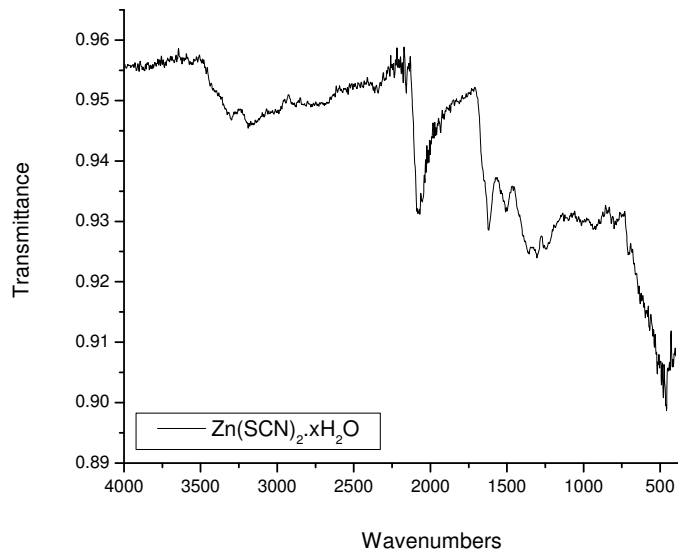
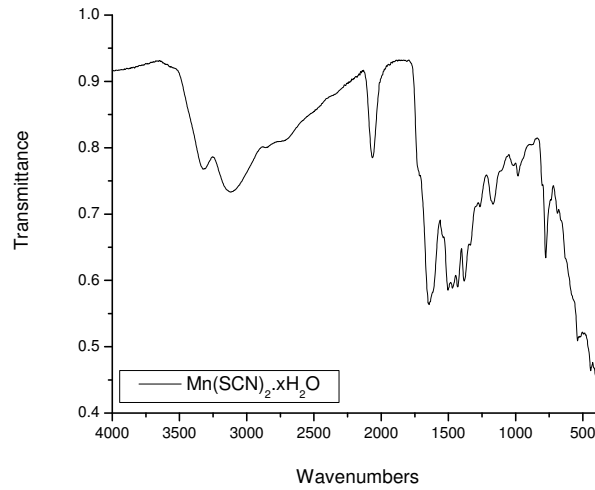
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Table 1: Infrared Frequencies (cm^{-1}) and Assignments for $\text{Mn}(\text{SCN})_2 \cdot x\text{H}_2\text{O}$, $\text{Zn}(\text{SCN})_2 \cdot x\text{H}_2\text{O}$ and $\text{Cd}(\text{SCN})_2 \cdot x\text{H}_2\text{O}$ formed in the reaction of MnCl_2 , $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or CdCl_2 salts with thiourea at 90°C .

$(\text{cm}^{-1})^a$			Assignments ^b
$\text{Mn}(\text{SCN})_2 \cdot x\text{H}_2\text{O}$	$\text{Zn}(\text{SCN})_2 \cdot x\text{H}_2\text{O}$	$\text{Cd}(\text{SCN})_2 \cdot x\text{H}_2\text{O}$	
2066	2069 s	2059 vs	$\nu(\text{CN})$; SCN
775 w	-	804 w, 704 w	$\nu(\text{CS})$; SCN
529 w	456 w	459 s	$\delta(\text{SCN})$; SCN
1163 w, 989 w	1243 w	1101w	$2X\delta(\text{SCN})$; SCN
3322, 3119 br	3300 vw	3372 m, 3287 ms	$\nu(\text{O-H})$; H_2O
1624 s	1623 vs	1628 vs	$\delta(\text{H}_2\text{O})$; H_2O

a: br, broad; m, medium; sh, shoulder; s, strong; w, weak

b: ν , stretching; δ , bending.



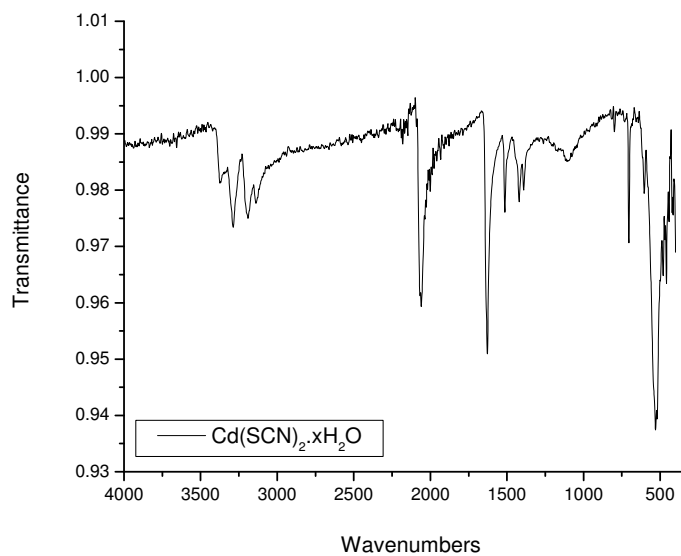


Fig. 1: Infrared Spectra of Mn(SCN)₂.xH₂O, Zn(SCN)₂.xH₂O and Cd(SCN)₂.xH₂O formed in the reaction of MnCl₂, Zn(NO₃)₂.6H₂O or CdCl₂ salts with thiourea at 90 °C.

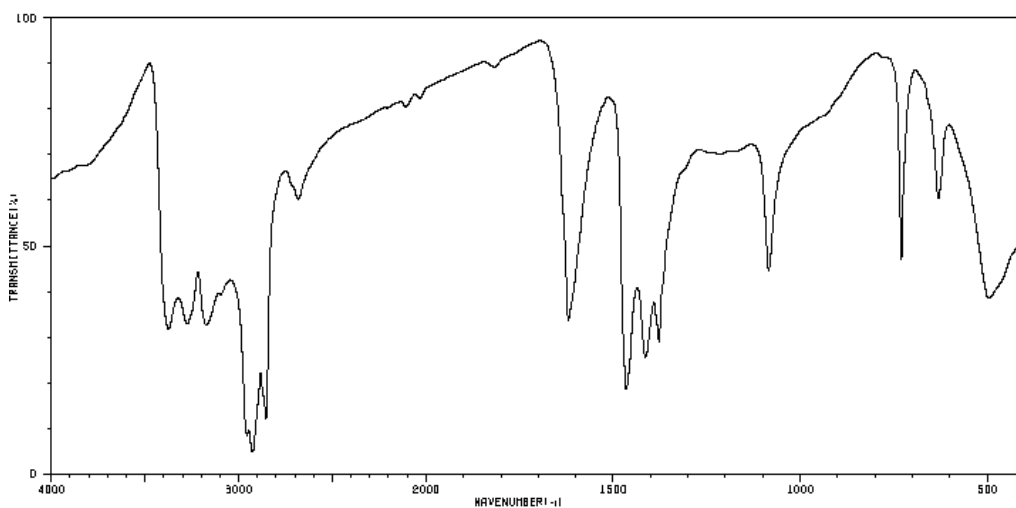


Fig. 2a: Infrared spectrum of thiourea ligand

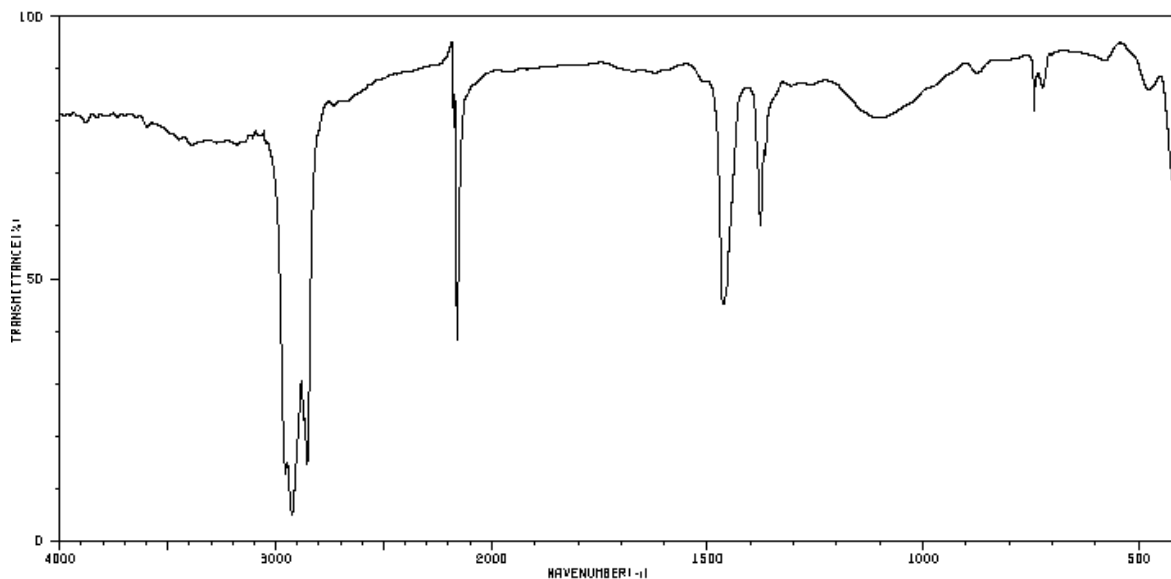


Fig. 2b: Infrared spectrum of $\text{Cu}(\text{SCN})_2 \cdot x\text{H}_2\text{O}$ commercial compound

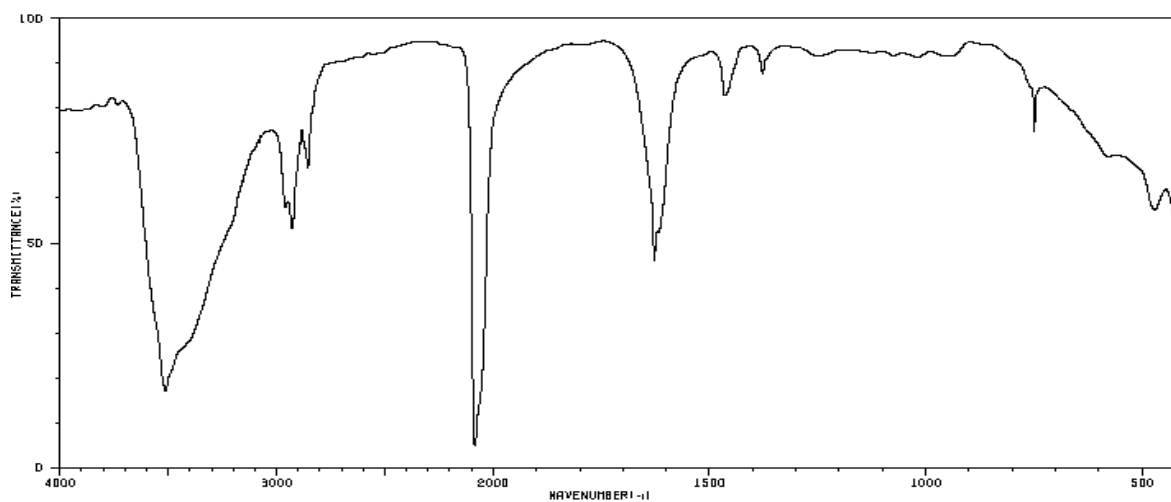


Fig. 2c: Infrared spectrum of $\text{Ba}(\text{SCN})_2 \cdot x\text{H}_2\text{O}$ commercial compound