

## Synthesis and Characterization of Organometallic Complexes of Thiocarbanilides and Substituted Thiocarbanilides–Using Manganese (II) Chloride

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### ABSTRACT

Organo-metallic complexes of substituted thiocarbanilide-using manganese (II) chloride were prepared, those were:-(1) 3:3'- Dichlorothiocarbanilide.Manganese (II) chloride. (2) 3:3'-dimethyl thiocarbanilide.Manganese(II)chloridee. (3) 2:2'- dimethyl thiocarbanilide.Manganese (II) chloride. Those compounds were colored, soluble in most organic solvents, insoluble in water, decomposed by hot solvents. The compounds (2) and (3) were spectrally characterized using UV and IR spectra, while the compound (1) was characterized by UV, IR, NMR and mass spectra. The molecular weight of the compound (1) was determined by three different methods; Rast's camphor method, mass spectra and the nitrogen contents. The stoichiometry of the reaction was found to be 2:1, and the coordination is from sulphur atom more than nitrogen.

**Keywords:** Organometallic complexes; Substituted Thiocarbanilides; Manganese (II) Chloride, IR; NMR.

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### INTRODUCTION

Thiocarbanilides have found their way into almost every branch of chemistry. It is a very commonly known industrial material. Commercially, they are used in dyes, photographic films, elastomers, plastics and textiles. Certain substituted thiocarbanilide are insecticides, preservatives, rodenticides, and pharmaceuticals [1]. In the academic field, thiocarbanilide is of great value in the characterization of organic compounds [1]. For example, advantage is taken of the fact that amines can easily be converted into solid sharp-melting substituted thiocarbanilides by allowing the aromatic amines to react with carbon disulfide to form symmetrical derivatives, and to react with an appropriate isothiocyanate to form unsymmetrical derivatives [1]. The ability of thiocarbanilide to form crystalline complexes with branched hydrocarbons, cycloaliphatic

structures and metals, has led to their use in the separation of mixtures of organic compounds, and metals [1].

The (C:S) group in thiocarbanilide may be considered as a functional analytical group for Ru and Os. A red colour with  $\text{OsO}_4$  is given by  $\text{CS}(\text{NPh})_2$  [2]. Re forms colored complex with diphenylthiourea in the presence of  $\text{SnCl}_2$  or  $\text{TiCl}_2$  and  $\text{HCl}$ , Re formed a very slightly soluble precipitate. The precipitate was soluble in  $\text{NaOH}$  and Re could be determined colorimetrically with  $\text{KSCN}$ . The formulas formed for Re organic compounds for rhenium diphenylthiourea chloride is  $[\text{ReO}_2\{\text{CS}(\text{NPh})_2\}_4]\text{Cl}_3$ .

It is certain that metallic salts add to thiocarbanilide and that these can be decomposed by heat, especially in alkaline solution to yield diphenylurea and metallic sulfide [3]. Definite additive compounds are formed when anhydrous solvents such as alcohol, methy-ethyl ketone or toluene are used. Thiocarbanilide mercuric chloride was prepared by adding slowly a cold alcoholic solution of thiocarbanilide to a cold alcoholic solution of mercuric chloride, in molecular equivalents [3]. A number of complex salts of thiocarbanilide with metallic halides have been prepared, Table 1 [3].

Although additive compounds were formed in the desulfurization of thiocarbanilide by copper hydroxide, with the use of concentrated Fehling solution, however, certain thiocarbanilide gave microcrystalline brilliantly colored compounds that could be isolated before copper sulfide was formed [4]. They proved to be additive compounds of one molecule of the thiocarbinilide with one molecule of copper hydroxide. The additive compound unite was  $\text{RNH.CS.NHR.Cu}(\text{OH})_2$ .

Thiocarbanilide on treatment, slowly with stirring, with a solution of  $\text{Cu}(\text{NO}_3)_2$  in  $\text{Me}_2\text{CO}$  gave the compound  $(\text{PhNH})_2\text{CS.CuOH}$  at room temperature, that was stable to cold dil.  $\text{HCl}$  and  $\text{NaOH}$  but decomposed by hot solutions, insoluble in  $\text{H}_2\text{O}$ ,  $\text{EtOH}$ , and  $\text{Me}_2\text{CO}$ , soluble in  $\text{CHCl}_3$ [5].

**Table 1. Thiocarbanilides and other metallic halides**

Composition $\text{T}=\text{C}_{13}\text{H}_{12}\text{N}_2\text{S}$	Colour	Crystal Form	M.P. C°
$\text{T}_2\text{CuBr}_2$	White	Prism	187
$\text{T}_2\text{. CdBr}_2$	Yellow	Rhomboids	140
$\text{T}_2\text{. HgI}_2$	White	Rhomboids	183
$\text{T}_2\text{. ZnCl}_2$	White	Prisms	172
$\text{T}_2\text{. AuCl}_3$	White	Prisms	194
$\text{T}_2\text{. SnCl}_4$	White	Prisms	260
$\text{T. As Br}_3$	White	Prisms	250
$\text{T. As I}_3$	Yellow	Prisms	250
$\text{T. HgI}$	Yellow	Prisms	139

The compound  $(\text{PhNH})_2\text{CS.CuCl}$  was obtained from the reaction of  $(\text{PhNH})_2\text{CS}$  and  $\text{CuCl}_2$  in absolute  $\text{EtOH}$  [5]. The other complexes which were prepared by that method, were  $(\text{PhNH})_2\text{CS.Cu}_2\text{SO}_4$  and  $(\text{PhNH})_2\text{CS.CuOAc}$  [6].

Complexes of diphenylthiourea with  $\text{BiCl}_3$ ,  $\text{AsCl}_3$ ,  $\text{SbCl}_3$ ,  $\text{CdCl}_2$  and  $\text{HgCl}_2$  have been synthesized and were fully characterized by elemental microanalyses and spectroscopic methods [7].

Dichloro (Bis[Diphenylthiourea]cadmium) complex have been used as the source of cadmium sulphide (CdS) nanoparticles. The reaction was carried out using hexadecylamine (HDA) as the solvent and stabilising agent for the particles.[8]

According to the IR spectra of  $\text{CuCl} \cdot 2\text{L}$  (L=diphenylthiourea), was suggested that Cu(I) is coordinated through S in all cases, except that of allythiourea [9].

The objective was the synthesis of organometallic compounds from thiocarbanilides and substituted thiocarbanilides using manganese (II) chloride, and the investigation of those compounds using spectroscopic tools to prevail the mechanism of the reaction.

## MATERIALS AND METHODS

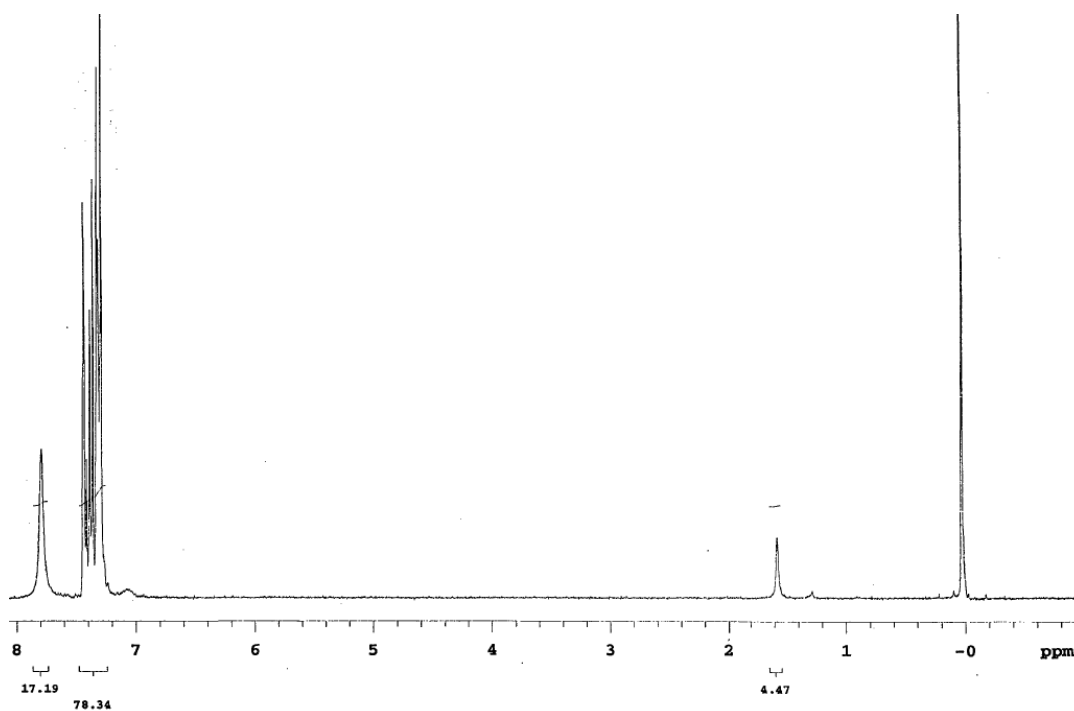
### 2.1 Physical Measurements:

Melting points were recorded. Perkin -Elmer Model 1330 infrared spectrophotometer was used. UV/VIS spectrophotometer model 550S was used for recording UV spectra.  $^1\text{H}$  nmr spectra and mass spectra were obtained by Lash Miller Chemical Labs. University of Toronto, Ontario, Canada.

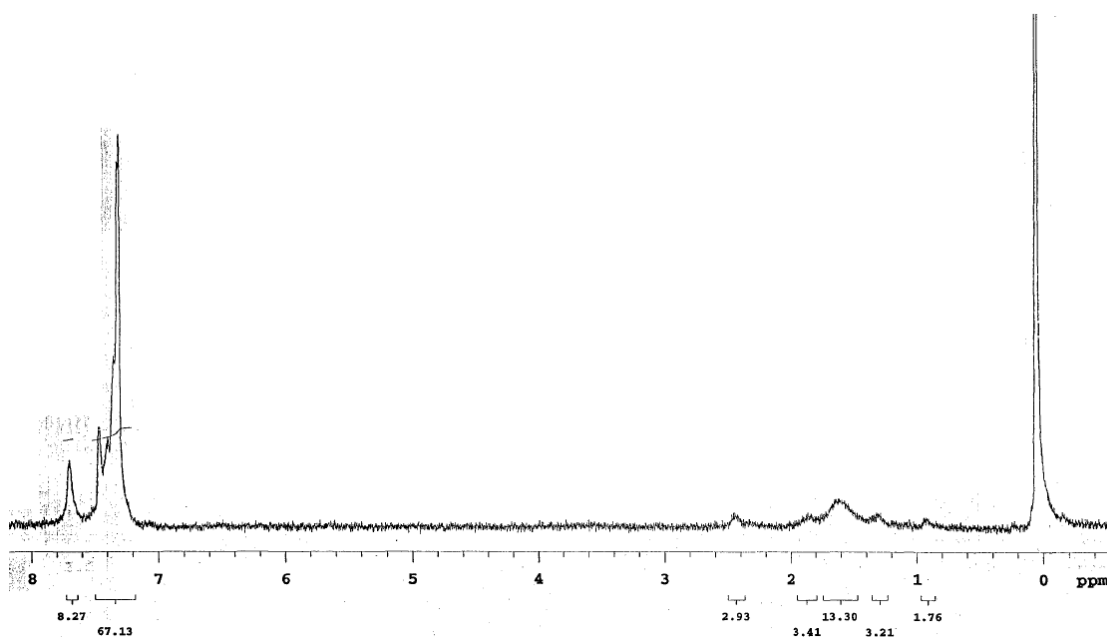
### 2.2. Preparation of Organometallic complexes of substituted thiocarbanilides using manganese (II) chloride:

#### (1) 3:3'-dichlorothiocarbanilide. $\text{MnCl}_2$ complex:

Manganese (II) chloride (0.66 gm) was dissolved in distilled water (20 c.c), and was added drop wise to a suspension of 3:3'- dichlorothiocarbanilide (1.0 gm) in distilled water (30 c.c.) placed in 500 c.c. Conical flask provided with stopper. And the turbid solution made acidic with 0.10 N HCl. The mixture was stirred for about an hour, the mixture remained clear for sometimes. Then an oily intermediate compound was formed, which turned into grey-green precipitate. It was filtered, washed with distilled water, drained well and dried. The yield was 63%, (m.p. 114-116°C), it decomposed by hot solutions, and was found to be insoluble in water, insoluble in petroleum ether, insoluble in dil HCl; soluble in ethanol, methanol, acetone and dimethoxy ethane (DME). The nitrogen content was found (7.77%, calc. 7.79%). The molecular weight was found (717.5, calc. 717);  $\nu_{\text{max}}$ .  $\text{cm}^{-1}$  (KBr) 3360 (N-H stretching) 3190, 3020 (aryl C-H), 1580, 1530, 1470 and 1420 (C=C), 1300 (-CS-NH amide II), 1250 (-CSNH- amide I), 1075 (C=S stretching), 960, 860 and 770 (C=CH aromatic), 670 (C-Cl),  $\lambda_{\text{max}}$ . (DME) 325nm ( $\epsilon = 748$ ); m/z 717 (49%), m/z less Cl 682 (58%), m/z less 2Cl=647 (70%), (Figures 1, 2 and 3);  $^1\text{H}$ nmr of this compound is blurred (spectrum 1 and 2).



<sup>1</sup>Hnmr spectrum 1: for the ligand 3:3'-dichlorothiocarbanilide



H'nmr spectrum.2: for complex: (3:3')dichlorothiocarbanilide)<sub>2</sub>.Manganese (II) chloride

**(2) 3:3'- dimethylthiocarbanilide.MnCl<sub>2</sub> complex:**

Manganese (II) chloride (0.38gm) was dissolved in distilled water (10. c.c), and was added drop wise to a suspension of 3:3'- dimethylthiocarbanilide (0.50 gm) in distilled water (20 c.c.) placed in 500 c.c. conical flask provided with stopper, the mixture was acidified with conc. HCl, and

stirred for about half and hour, then blue crystals were formed. The product was filtered Washed with water and dried. The yield was 57.6% (m.p. 93-96°C). It was decomposed by hot solutions, and was found to be insoluble in water, insoluble in petroleum ether, insoluble in dil HCl, soluble in ethanol, methanol, acetone and dimethoxy ethane (DME).  $\nu_{\max}$ .  $\text{cm}^{-1}$  (KBr) 3360 (N-H stretching), 3160 (aryl C-H), 2960 (CH<sub>3</sub>), 1580, 1500 (C=C), 1340 (CS-NH- amide II), 1280, 1220 and 1160 (-CSNH- amide I), 1080 (C=S stretching) 780, 720 and 680 (C=CH aromatic);  $\lambda_{\max}$ . (DME) 334nm ( $\epsilon$  =924).

### (3) 2:2'-dimethylthiocarbanilide.MnCl<sub>2</sub> Complex:

Manganese (II) chloride (0.165gm) was dissolved in distilled water (5 c.c.), and was added drop wise to a suspension of 2:2'- Dimethylthiocarbanilide (0.20gm) in distilled water (10 c.c.) placed in 250 c.c. conical flask provided with stopper, the mixture was acidified with conc. HCl, and stirred for about an hour, then greyish crystals were formed. The product was filtered, washed with water and dried. The yield was 53.8%. (m.p. 155-165°C), it was found to be soluble in ethanol, methanol, acetone and DME; insoluble in water and dil HCl. It was decomposed by hot solutions,  $\nu_{\max}$ .  $\text{cm}^{-1}$  (KBr) 3320 (N-H stretching), 3140 (aryl C-H), 2950 (CH<sub>3</sub>), 1520 (C=C), 1320 (-CS-NH-amide II), 1260, 1240 and 1210 (-CSNH-amid I), 1100 (C=S stretching), 920, 760, 740 and 720 (C=CH);  $\lambda_{\max}$  (DME) 336nm ( $\epsilon$  =805).

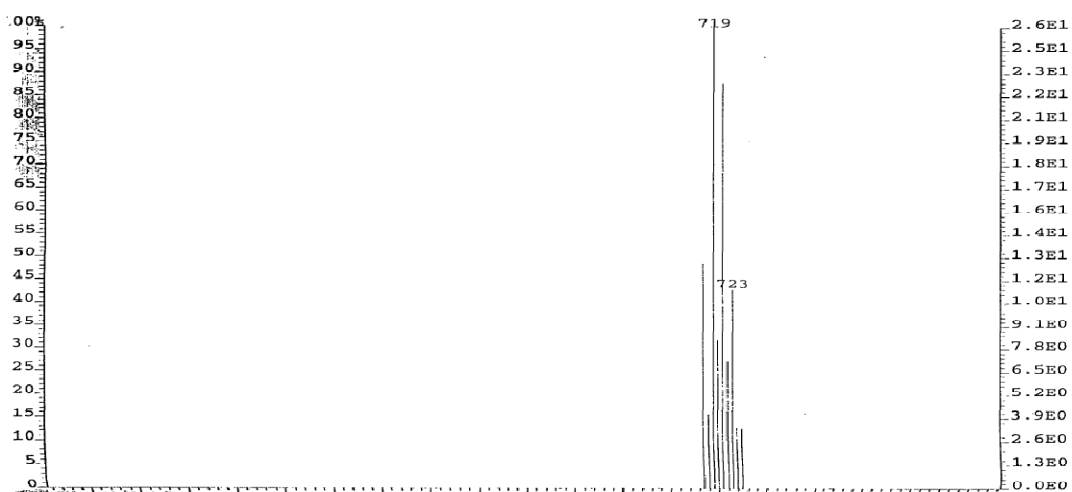


Figure 1. Calculated distribution for molecular weight for compound (1)

## 2.3 Reaction of thiocarbanilide (diphenylthiourea) and manganese (II) chloride in different media:

**2.3.1** To the mixture of thiocarbanilide (1.0 gm) and manganese (II) chloride (0.5gm) in absolute ethanol (50 c.c.) a solution of sodium hydroxide (40%) was added slowly. The mixture darkened and a faint yellow oil was formed.

**2.3.2** The mixture of thiocarbanilide (0.50gm) and manganese (II) chloride (0.5 gm) were refluxed in aqueous medium acidified with conc. HCl as catalyst, the hydrogen sulphide was evolved and white precipitate was formed. The precipitate was void of sulphur according to Lassaigne's test.

**2.3.3** When the mixture of thiocarbanilide (0.5 gm) and manganese (II) chloride (0.2 gm) were refluxed in absolute ethanol (50 c.c.), no hydrogen sulphide was evolved, and no precipitate was formed.

**(3:3'-dichlorolthiocarbanilide)<sub>2</sub>.Manganese(II)chloride**

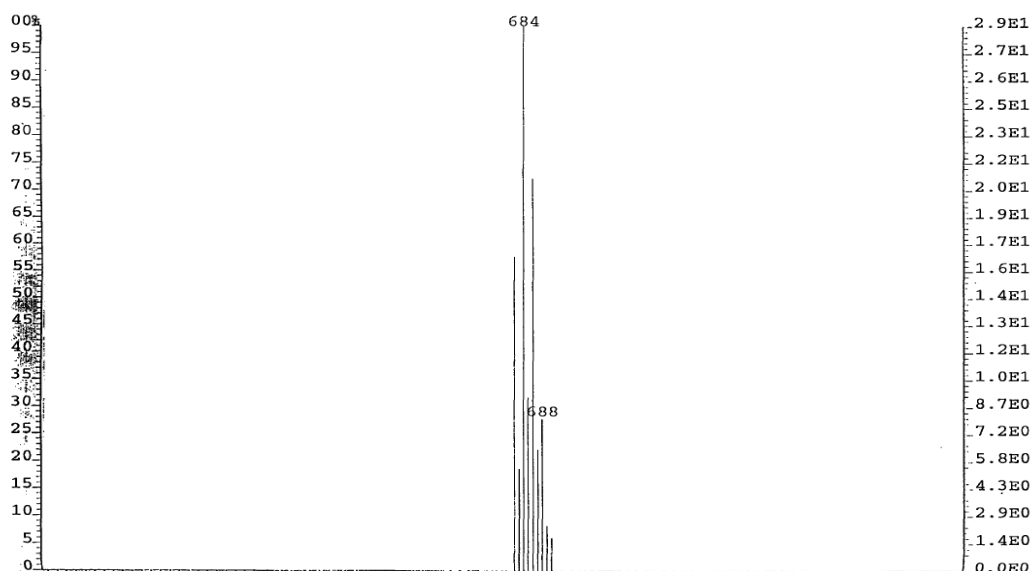


Figure 2.m/z less Cl for compound (1) (3:3-dichlorothiocarbanilide)<sub>2</sub>.Manganese (II) chloride

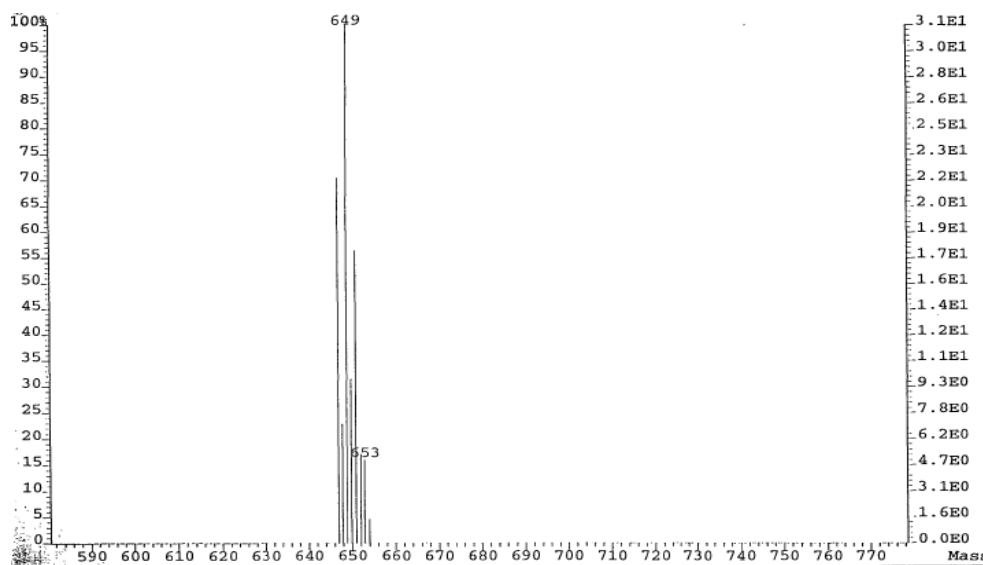


Figure 3.m/z less 2Cl for compound (1) (3:3-dichlorothiocarbanilide)<sub>2</sub>.Manganese (II) chloride

## RESULTS AND DISCUSSION

### Reaction of unsubstituted thiocarbanilide with MnCl<sub>2</sub> in different media:

**3.1.1** The reaction between diphenyl thiourea (DPTU) and manganese (II) chloride in absolute ethanol in the presence of 40% NaOH as a catalyst, led to the formation of a faint-yellow

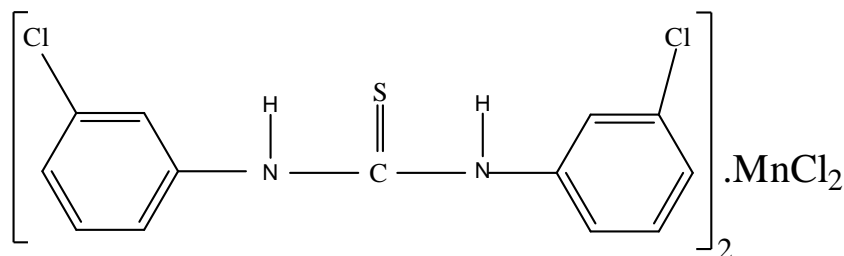
unseparable oil. According to the literature review [10] desulfurization of thiocarbanilide took place by  $\text{Cu}(\text{OH})_2$  and  $\text{Pb}(\text{OH})_2$  forming dark colour of metal sulphide and yellow oil which might be isothiocyanate ( $\text{PhNCS}$ ).

**3.1.2** The reaction between compound (DPTU) and manganese (II) chloride in aqueous medium acidified with conc. HCl, led to the liberation of hydrogen sulphide, and formation of white precipitate, no sulphur was present in the precipitate according to the lassange's test. Literature review [3] explained that thiocarbanilide was easily oxidized in acidic solution by various reagents e.g.  $\text{KMnO}_4$ ,  $\text{KOBBr}$ , etc. and gave good yield of diphenylurea, i.e. the primary effect of oxidizing agent to substitute the sulphur atom by oxygen, thus yielding diphenylurea.

**3.1.3** In none aqueous acidified medium - absolute ethanol / conc HCl no reaction took place between compound (DPTU) and manganese (II) chloride.

### 3.2 Reaction of substituted thiocarbanilide, 3:3'-dimethylthiocarbanilide, 2:2-dimethylthiocarbanilide and 3:3'-dichlorothiocarbanilide with manganese (II) chloride:

3.2.1 The above compounds were oxidized by manganese (II) Chloride in aqueous acidic media. In each case the reaction gave the manganese (II) chloride complexes in fairly good yields, (1) 63%, (2) 57.6% and (3) 53% respectively, which were colored, decomposed by hot solutions, soluble in most organic solvents, insoluble in distilled water. The grey-green complex (1) which molecular weight was 717, gave an m/z (717), m/z less Cl (682) and m/z less 2 Cls (647) (Figure 1, 2 and 3), from this the molecular formula of the complex (1) should be  $(3:3'\text{-dichlorothiocarbanilide})_2 \cdot \text{MnCl}_2$ , as can be explained below:



This proved that the complexes were formed by the reaction of two molecules of 3:3'-dichlorothiocarbanilide and one molecule of manganese (II) chloride, i.e. the stoichiometry of the reaction is 2:1.

The ultraviolet spectra showed that the  $\lambda_{\text{max}}$  of the substituted thiocarbanilide were in the range 281-286 nm (Table 2), and the ultraviolet spectra of the complexes were in the range 325-336 nm (Table 2). The absorption of  $\lambda_{\text{max}}$  in the thiocarbanilide was based on the conjugation of the benzene ring, and the lone pair of the nitrogen atom and the two pairs of the functional group  $\text{C}=\text{S}$ , the increase in the  $\lambda_{\text{max}}$  in the complexes was an indication of the formation of the complexes on those two atoms ( $-\text{N}-$  or  $\text{C}=\text{S}$ ), (Table 2).

The shift in the IR spectra of the coordinated ligands could be used to indicate the mode of bonding of the organic ligands in those compounds. The infrared spectra of the complexes showed a clear N-H stretching frequency at  $3360 \text{ cm}^{-1}$ , as that of the free ligands, hence there



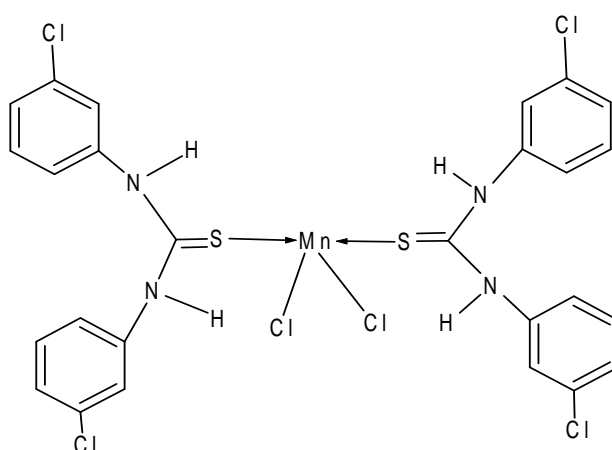
was no manganese-nitrogen bond formed. The C=S stretching frequency of complexes (1), (2) and (3) appeared at  $1300\text{ cm}^{-1}$ ,  $1340\text{ cm}^{-1}$  and  $1320\text{ cm}^{-1}$  respectively, while C=S stretching frequency of ligands were observed at  $1305\text{ cm}^{-1}$ ,  $1350\text{ cm}^{-1}$  and  $1330\text{ cm}^{-1}$ , which were shifted down by  $5\text{ cm}^{-1}$  and  $10\text{ cm}^{-1}$ . That supported the fact of the coordination of the sulfur atom to manganese (II).

**Table 2. U.V. and visible spectra maxima for substituted thiocarbanilide and the complexes of substituted thiocarbanilide.MnCl<sub>2</sub>**

Compound	Concentration in mole/dm <sup>3</sup>	$\lambda_{\text{max}}$ in nm	Absorbance	$\epsilon$
S-Di-m-chlorothiocarbanilide	0.00010	283	1.520	15200
S-Di-m-chlorothiocarbanilide.MnCl <sub>2</sub>	0.00139	325	1.040	748
S-Di-m-tolythiourea	0.00010	281	1.800	18000
S-Di-m-tolythiourea.MnCl <sub>2</sub>	0.00157	334	1.450	924
S-Di-o-tolythiourea	0.00011	286	1.149	11490
S-Di-o-tolythiourea.MnCl <sub>2</sub>	0.00130	336	1.046	805

<sup>1</sup>Hnmr of the ligand compound 3:3'-dichlorothiocarbanilide (spectrum 1) was clear and acceptable, but the <sup>1</sup>Hnmr of the complex (1) 3:3'-dichlorothiocarbanilide.MnCl<sub>2</sub> (spectrum 2) was blurred. The <sup>1</sup>H NMR spectra of ligand 3:3'-dichlorothiocarbanilide (spectrum 1) showed signals at 7.28-7.44 ppm due to equivalent ring protons (aromatic protons). While the complex showed those signals at a wide range field than the ligand (7.26-7.48 ppm) of minor difference since aromatic ring protons became magnetically un-equivalent for that ligand. The complex showed signal due to NH proton (7.70 ppm), while free ligand diphenylthiourea showed a single resonance at 7.78 ppm (low field).

The mass spectrum of the complex (1) 3:3'-dichlorothiocarbanilide.MnCl<sub>2</sub> gave an accurate m/z, m/z less Cl and m/z less 2Cl (Figures 1, 2 and 3). From the fact that sulphur is a highly donating atom as compared to nitrogen atom, basic, it can be concluded that the donation is from sulphur more than nitrogen, and the proposed structure of 3:3'- dichlorothiocarbanilide.MnCl<sub>2</sub> complex (1) could be as follows:



The same inner sphere complex structure could stand for compound (2) and (3). The substituent effect of the chlorine in meta-position in compound (1) and the meta-methyl in compound (2)



gave comparable percentage yield. That result was probably due to the fact that both chlorine atom and the methyl group have comparable polarizability, mesomeric and inductomeric, effects. These polarization effects whatever their direction, reduce the energy of the system and so stabilize it. Besides steric hindrance might have reduced more the yield in compound (3).

### CONCLUSION

The organometallic complexes of substituted thiocarbanilide – using manganese (II) chloride, which were synthesized had inner sphere complexes, that were unstable in hot solvents. Since gold salt and copper salt of thiocarbanilide have antituberculous activity, and copper complexes of thiocarbanilides have an antiphenoloxidase activity, the synthesized manganese (II) chloride inner sphere complexes, could have biological activity; Besides, substituted thiocarbanilides can be used as analytical reagent for separation of manganese or manganese halides in acidic aqueous media.

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