Organometallic Complexes of Thiocarbanilides And Substituted Thiocarbanilides – Using Manganese (II) Chloride

By

Musa Elballa Mohamed Babiker

B. Sc. Chemistry

A thesis submitted in fulfilment for the M. Sc. Degree in

Chemistry

2000

Department of Chemistry

Faculty of Science

University of Khartoum

Dedication

To members of my family

And to

Samia Khalid

ACKNOWLEDGEMENTS

My praise and thanks go to "ALLAH", who gave me the health and strength to make this research.

I would like to express my gratitude to my supervisor, Dr. Christina Yagoub Ishag, for her support, guidance and encouragement through this work.

My thanks also go to Huda Henry Riyad, University of Toronto, Ontario, Canada, for making H'nmr and mass spectra, which were reported in this work.

Special thanks to Samia Khalid for her encouragement to complete this research work.

ABSTRACT

Organo-metallic complexes of substituted thiocarbanilide-using manganese (II) chloride were prepared, these are:-

(VIII) 3:3'- Dichlorothiocarbanilide. Manganese (II) chloride.

(IX) 3:3'- dimethyl thiocarbanilide. Manganese (II) chloride.

(X) 2:2'- dimethyl thiocarbanilide. Manganese (II)chloride

These compounds are coloured, soluble in most organic solvents, insoluble in water, decomposed by hot solvents.

The physical properties of the compounds (IX) and (X) were studied by UV and IR spectra, and the physical properties of the compound (VIII) were studied by UV, IR, mass spectra and NMR.

The molecular weight of the compound (VIII) 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.

THIS PAGE IS MISSING
IN THE
ORIGINAL DOCUMENT

CONTENTS

Chapter One

INTRODUCTION AND LITERATURE REVIEW

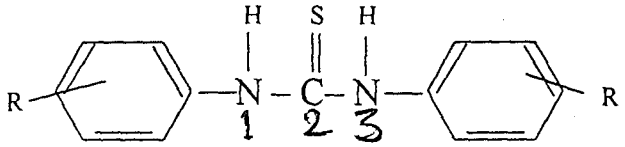
Thiocarbanilides have found their way into almost every branch of chemistry. It is a very commonly known industrial material. Commercially, they are used in dyes, photographic film, elastomers, plastics and textiles. Certain substituted thiocarbanilide are insecticides, preservatives, rodenticides, and 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 isothiocynate to form unsymmetrical derivatives[1].

The ability of thiocarbanilide to from 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].

Because of the great versatility of these compounds, it was necessary to set definite limits to the scope of this review with respect to the literature sources, types of thiocarbanilide, their properties and their uses [1].

Thiocarbanilide has alternative name diphenylthiourea. The nomenclature used is that designated by Chemical Abstracts. The thiocarbanilide system is numbered as shown below:



R= CH_3,C_2H_5, CH_3O, Cl, Br, I, NO_2,NH_2,OH,COOH, H

If R is present in the ring, it is called 1,3-di-substituted thiocarbanilide.

With regard to applications, chemical, optical and biological properties of thiocarbanilide are considered.

1.I Chemical properties of thiocarbanilides

1.I.1 In analysis:

The (C:S)group in thiocarbanilide may be considered as a functional analytical group for Ru and Os. A red colour with OsO_4 is given by $CS(NHPh)_2$ [2]. Re forms coloured complex with diphenylthiourea in the presence of $SnCl_2$ or $TiCl_2$ and HCl, Re formed a very slightly soluble precipitate. The precipitate was soluble in NaOH and Re could be determined colorimetrically with KSCN. The sensitivity of this method was O.15 γ/ml. The formulas formed for Re organic compounds for rhenium diphenylthiourea chloride is $[ReO_2\{CS(NHPh)_2\}_4]Cl$ [3].

Small amounts of tellurium was determined spectrophotometrically with sym-diphenylthiourea. Te is extracted almost quantitatively from 4.5-8.0 M HCl or $HClO_4$ solutions with a $CHCl_3$ solution of diphenylthiourea, and up to 200 γ of Te can be determined by measuring the absorbance of the yellow complex in the $CHCl_3$ phase at a wave- length between 380 and 410 mμ [4].

1.1.2 As catalyst:

Effect of diphenythiourea on the polymerization of methyl methacrylate with various organic peroxides as initiator [5].

The effect of diphenylthiourea (DPTU) on the radical polymerization of methyl methacrylate (MMA) has been studied in benzene solution at 50°C with use of cumene hydroperoxide (CHP), P-menthane hydroperoxide (PMHP), tert-butyl perbenzoate (tBPBz), di-tert-butyl peroxide (DBP), and dicumyl peroxide (DCP) as initiators. In the CHP - initiated polymerization, the rate of polymerization increased appreciably on addition of DPTU with a linear dependence on the square root of DPTU concentration up to a maximum which was observed when the ratio of the concentration of CHP to DPTU was 2.5 [5]. Then the rate decreased gradually with increasing DPTU concentration in the range greater than the above ratio [5]. It was thought that the acceleration effect observed was due to

a redox reaction caused by the interaction of a peroxide-monomer and/ or a peroxide-solvent complex with DPTU, and the decrease in the polymerization rate which was observed over a certain concentration of DPTU was due to the action of the oxidized product of DPTU as a transfer agent [5]. The effect of substituent was studied by using para and meta-substituted DPTU.

It was found that the polymerization rate increased as electron donating substituents are added to the benzene ring of DPUT with considerable dependence on Hammett's equation (P = -0.36) [5].

As catalyst in discolouration of autoxidized fish oil, N, N'-di-o-tolythiourea, N-phenyl-N'-O-tolythiourea and N,N'-diphenylthiourea catalytically promoted discolouration of autoxidized fish oil [6].

1.1.3. As antioxidant:

Thiocarbanilide can be used as antioxidant for Lubricating oils.

It was found that thiocarbanilide react readily with steal surface, with rate of the reaction increasing at higher pressure. A microscopic study of the lubricated surfaces showed that the action of thiocarbanilide causes the formation of grooves in the direction of the rotation, the simultaneous presence of this element causes the formation of a porous surface that can hold the oil even at high pressure and thereby lubricates itself [7].

Thiocarbanilide was more effective as antioxidant for corbic acid inhibition of the autoxidation of oils and fats.

1.1.4. Toxicity:

Administrated intragastrically to rabbits, $CS(NHPh)_2$ was found to be physiologically active and toxic, the minimal fatal dose being 1.5g / Kg. $CS(NHC_6H_4Me.O)_2$ was found to be about half as toxic. Cats appeared to be more susceptible to these compounds than rabbits. [1]

It is suggested that toxicity is related to metabolic loss of S [8].

1.2 Optical properties of substituted thiocarbanilide:

Substituted thiocarbanilides are useful for characterization of primary and secondary amines. To enhance this usefulness, and particularly to make it possible to distinguish more readily between members of homologous series, the optical properties of these substances have now been studied. The symmetrical substituted thiocarbanilides were prepared from aromatic amines and carbon disulfide; the unsymmetrical from phenyl isothiocynate and various amines. Their melting points, which are in reasonable agreement with the values recorded in the literature [9].

The optical properties of a number of substituted thiocarbanilide have been determined and have been shown to be useful in distinguishing

between members of a homologous series, particularly when these have very nearly identical melting points [9].

1.3 Preparation of thiocarbanilides:

There are several common syntheses for thiocarbanilides, many variations have been applied to each of these when circumstances demanded it. As might be expected, certain advantages and disadvantages arise from the use of any one of the following methods of preparation [10].

1.3.1 Carbon disulfide and an amine

$$CS_2+2RNH_2 \longrightarrow RHNCSNHR+H_2S$$

The reaction shown in the above equation is the common way of describing the overall reaction of primary amines with carbon disulfide to give substituted thiocarbanilide [10]. It does not, however, tell the whole story. Many theories concerning the mechanism of this reaction have been published, and the conclusions are somewhat conflicting. Considering the experimental data, which have been presented, the most reosonable course for the reaction seems to be [10].

(1) $RNH_2 + CS_2 \rightleftharpoons RHNC(=S)SH$

(2) $RHNC(=S)SH + RNH_2 \rightleftharpoons (RHNCS)^- (NRH_3)^+$

(3) $(RHNCS)^- (NRH_3)^+ \xrightarrow{\text{heat}} RNCS + RNH_2 + H_2S$

(4) $RNCS + RNH_2 \longrightarrow RHNCSNHR$

$2RNH_2 + CS_2 \longrightarrow RHNCSNHR + H_2S$

while primary amines give 1,3 – disubstituted thioureas with carbon disulfide, secondary amines and carbon disulphide do not give the corresponding tetrasubstituted compounds.

In this method there is a further evidence of the presence of the isothiocyanate, is that when the reaction of amine and carbon disulfide is carried out in alcoholic medium and the reaction time is lengthy, thiourethans are sometimes formed as well as the desired product [10].

Although the equation indicates that theoretically two moles of amine should be used per mole of carbon disulfide, it is usually wise to use an excess of the latter in view of its high volatility.

Alcohol or benzene may be used in the reaction as solvent for the starting materials or to raise the reaction temperature [10].

The most common application of this method is to synthesize sym. and unsymmetrical 1,3 – disubstituted thioureas.

A major drawback in using this method for the preparation of 1,3-disubstituted thioureas is that it is often very slow. For example, it was found necessary to warn m- nitroaniline and carbon disulfide for 200hrs in forming the disubstituted thiourea. Several means have been successfully employed to accelerate this reaction [10].

1.3.1.1. Addition of potassium or sodium hydroxide:

The most obvious way to accelerate this reaction is to remove the hydrogen sulfide by adding a base such as sodium or potassium hydroxide[10].

This can be done by adding either an ethanolic or an aqueous solution of the hydroxide to the mixture of carbon disulfide and the amine[10]. The latter is preferable, since the presence of alcohol may lead to the formation of side products, especially thiourethans [10]. Optimum results are achieved by combining equimolar quantities of amine, carbon disulfide and aqueous 40 percent sodium (or potassium) hydroxide, with cooling and agitation. In general, the yields are excellent.However, the method dose not

work with some amines, e.g., O- and P- chloroaniline and O-, M-, and P-nitroaniline [10].

1.3.1.2. Addition of Iodine and pyridine:

Pyridine was found to promote the reaction by forming an unstable addition product with hydrogen sulfide

$$C_6H_5N + H_2S \rightleftharpoons C_5H_6N.H_2S$$

More impressive results were obtained by adding the calculated amount of iodine to solution of the amine in carbon disulfide and pyridine. The iodine eliminated the hydrogen sulfide by the reaction [10],

$$H_2S + I_2 \longrightarrow 2HI + S$$

And the hydrogen iodide, was in turn, removed from the solution by conversion to pyridinium iodide, which is insolube in carbon disulfide [10]. The overall reaction is:

$$2RNH_2 + C_2S + I_2 + 2C_6H_5N \longrightarrow (RNH_2)_2CS + 2C_6H_5N.HI + S$$

Using this procedure, thiocarbanilides from such amines as aniline, O, M- and P- chloroaniline, m-nitroaniline, and M- and P- aminobenzoic acid were obtained in yields of 75-99 percent. Especially impressive was the good yield of thiocarbanilide obtained from m-nitroaniline in 3 hr. as compared to the 200 hr. required for a poor yield when no catalyst was added [10]. In further studies, the relative reaction rates of halo-substituted anilines were found to be o > m > p and I > Br > Cl [10].

Best results are obtained when the reactants are used in the following ratio: 2.0 moles of amine: 1.0 mole of iodine: 4.0 moles of pyridine: 3,000 ml. of carbon disulfide [10].

The reaction is complete when the colour of iodine has disappeared and the pyridinium iodide has completely precipitated. The mixture is then steam–distilled until all traces of carbon disulfide and pyridine are gone.

Pyridinium iodide is easily removed by washing with water and the product is purified by recrystallization.

1.3.2.. Thiophosgene and amine:

Primary amines react with thiophosgene to give a 1,3-disubstituted thiourea [10].

$$CSCl_2 + 2RNH_2 \longrightarrow RHNCSNHR + 2HCl$$

The mechanism of this reaction has been explained in the following manner:

(1) $RNH_2 + CSCl_2 \longrightarrow (RHNHClCSCl) \longrightarrow RHNCSCl + HCl$

(2) $RHNCSCl \longrightarrow RNCS + HCl$

(3) $RNCS + H_2NR \longrightarrow RNHCSNHR$.

Preparation of the thiocaranilide by this method is best carried out by refluxing one mole of thiophosogene with two moles of the amine in an aqueous, chloroform-aqueous or acetone aqueous medium [10]. When thiophosgene no longer appears in the reflux condenser, a mole of potassium carbonate is added and the heating continued for several hours, the product is then isolated and purified in a manner appropriate to the particular compound [10].

1.3.3. Special synthesis of thiocarbanilide:

This method is specific for a single compound, while others are of a general nature.

Thiocarbanilides derivatives can be prepared by heating a primary amines with a salt of trithiocarbonic acid [14].

Heavy metal salts have been especially recommended. This method appears to have little advantage over method A and requires more steps.

$2CS + 2C_6H_5NH_2 + NaOH \longrightarrow SC(NHC_6H_5)_2 + Na_2CS_3 + H_2O$

$Na_2CS_3 + MCl_2$ aq. medium $\longrightarrow MCS_3 + 2NaCl$ (M = heavy metal)

$MCS_3 + 2RNH_2 \longrightarrow CS(NHR)_2 + MS + H_2S$

However, an interesting variations is

$$Na_2CS_3 + 2ArNO + H_2O \longrightarrow SC(NHAr)_2 + Na_2S_2O_3$$

This has been successfully used in preparing, 1,3-bis (4-hydroxyphenyl) and 1,3 bis (4-dimethy aminophenyl) thiourea from 4-nitrosophenol and 4-nitroso-dimetlylaniline, respectively [10].

1.4 Reactions of Thiocarbanilide:

Although thiocarbanilide is a very commonly known industrial material , its chemical properties have not been studied exhaustively. This review contributes to the knowledge of its oxidations, nitrations, capacity to form additive compounds and other different reactions [11].

1.4.1 oxidation Reactions:

Various oxidation in acid and neutral solutions have been effected, the primary effect of oxidizing agents is to substitute the sulfur atom by oxygen, thus yielding diphenylurea, a compound leading itself easy

separation and identification. When acid solutions are employed thiocarbanilide tends to yield aniline, phenyl mustard oil and triphenlguanidine, alkaline oxidizing reagents avoid these by-products [11].

Oxidations were effected by various reagents, most of which gave good yields of diphenylurea, but the sodium peroxide method excels in simplicity of separation and yield of pure product. Some of the reagents separate free sulfur, and others oxidizing it to alkali sulfate, Table 1 [11].

TABLE 1

Other alkaline oxidations

Reagent	**T**	**Sulfur**	**Yield of $(C_6H_5NH)_2CO$,%**
$KMnO_4$	Room	$S+Na_2SO_4$	Good
K_2CrO_4	100	$S+Na_2SO_4$	70 – 80
$K_2S_2O_8$	Room	S	75
CaCl(ClO)	Room	$CaSO_4$	Poor
KOBr	Room	K_2SO_4	Good
KOI	Room	K_2SO_4	Good

From the forgoing it is evident that thiocarbanilide is smoothly oxidized by alkaline oxidants to diphenylurea, the sulfur there of being precipitated or oxidized to sulfate [11].

Thiocarbanilide is also oxidized to diphenylurea by nitric acid, nitration then yielding either dinitro- or tetranitro-diphenylurea and hexanitro-diphenylurea from thiocarbanilide are given [11].

Thiocarbanilide can be oxidized by diacylperoxides in petroleum ether to give bis (N, N'-diphenylformamidine) disulfide [12].

The oxidation of thiocarbanilide by Cu (II) in acetonitrile has been investigated. In most cases, a 1:1 stoichiometry is observed. The reaction proceeds with formation of a red complex which was found by E. S. R., to be a paramagnetic Cu(II). Thiocarbanilide complex which shows no evidence for Cu-N in plane bonding [13].

1.4.2 Addition Reactions

Various desulfurizing reagents have been employed in contact with thiocarbanilide as, for example mercuric oxide, lead acetate, etc. [11]. The casual view is that double decomposition results in the process, however, closer study indicates that addition reactions are involved. That the addition is not on nitrogen is precluded by the inability of diphnylurea to form corresponding additive compounds [11]. That the addition is on the sulfur atom seems the alternative conclusion.

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 [11].

Definite additive compounds are formed when anhydrous solvents such as alcohol, methy-ethyl ketone or toluene are used [11].

Thiocarbanilide mercuric chloride, was prepared by adding slowly a cold alcoholic solution of thiocarbanilide to a cold alcoholic solution of mercuric chloride, in moleculer equivalents [11].

A number of complex salts of thiocarbanilide with metallic halides have been prepared, Table 2 [11].

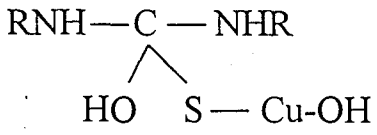
Table 2

Thiocarbanilide and other metallic halides

Composition $T=C_{13}H_{12}N_2S$	**Colour**	**Crystal Form**	**M.P.C°**
T_2CuBr_2	White	Prism	187
T_2. Cd Br_2	Yellow	Rhomboids	140
T_2. Hg I_2	White	Rhomboids	183
$T_2.ZnCl_2$	White	Prisms	172
T_2. $AuCl_3$	White	Prisms	194
T_2. $SnCl_4$	White	Prisms	260
T. As Br_3	White	Prisms	250
T. As I_3	Yellow	Prisms	250
T. HgI	Yellow	Prisms	139

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 coloured compounds that could be isolated before copper sulfide was formed[14]. They proved to be additive compounds of one molecule of the thiocarbinilide with one molecule of copper hydroxide. The additive

compound unite as RNH.CS.NHR.$Cu(OH)_2$ and can be depicted structurally as follows [14].



By the new analytical method, was found that thiocarbanilide reacted with alk. K_2 Hg I_4 gave yellow complex, which has the formula C_{26} H_{20} Hg_3 I_2 N_4S_2 [15].

The reaction was carried out in a H_2O-EtOH mixture [15].

Copper derivatives of 1,3 diphenyl-2-thiourea were prepared. $(PhNH)_2CS$ were used as coordinating ligands [15]. $(PhNH)_2CS$. CuOH was prepared by adding a solution of $Cu(NO3)_2$ (2 g.) in Me_2CO slowly with stirring to 4 g. thiocarbanilide in Me_2CO at room temperature, which was stable to cold dil. HCl and NaOH but decomposed by hot solutions, insoluble in H_2O, EtOH, and Me_2CO, soluble in $CHCl_3$. $2(PhNH)_2$ CS. CuCl was prepared by adding slowly $CuCl_2$ (2g.) in absolute EtOH to 4g. $(PHNH_2)$ CS in absolute EtOH.

The other complexes which were prepared by this method, were $2(PHNH_2)CS.Cu_2SO_4$, $4(PHNH)_2CS.Cu_2SO_4$ and $(PHNH_2)$ CS.CuOAc[16].

1.4.3 Different Reactions:

Thiocarbanilide can be reacted with ACNNaph in CS_2 to give the Na salt of thiocerbanilide, pale yellow, m.p. 70°c, in contact with the skin it causes a severe form of eczema [17]. Reaction of $(PhNH)_2CS$ with S under pressure is as follows [18].

$(PhNH)_2CS+S \longrightarrow C_6H_4.S.C(NHPh): N+H_2S \longrightarrow C_6H_4.S.C(SH): N+PhNH_2$

Irrespective of the solvent, the primary reaction between $(PhNH)_2CS$ and monochloroacetic acid is the formation of diphenylisothiohydantion [19]. The best yield were obtained with short heating, a small ratio of solvent to reactants, a slight excess of $ClCH_2CO_2H$ and the addition of sufficient AcONa to remove the HCl from the reaction as rapidly as formed [19].

Thiocarbanilide can be refluxed with sulphur monochloride to give 2-anilinobenzothiazole m.p. 159°C, Ac derivative, m.p. 162°C [20].

Thiocarbanilide can be reacted with carbon disulfide and sulfur to give mercuptobenzothiozole which is used as vulcanization accelerators [21].

Thiocarbanilide can be condensed with phenylacetaldehyde on heating and addition of C_6H_6 to the cold mixture gave 3-phenyl-4-anilinoquinoline, m. 181°C, HCl salt m.p. 320°C, Picrate M.P. 248°C [22]. The mechanism of the condensation is proposed as follows:

(1) $(PhNH_2)\ CS \longrightarrow PhNH_2+PhNCS$

(2) $PhNH_2 + PhCH_2CHO \longrightarrow H_2O + Ph:CHCH_2Ph$

(3) $Ph:CHCH_2Ph + PhNCS \longrightarrow$ 3-phenyl-4-anilinoquinoline + H_2S

Although thiocarbanilide can be condensed with malonyl chloride $[CH_2(COCl)_2]$ to give crude product, which can extracted with CS_2 to give 1,3-diphenyl-2-thiobarbituric acid, m.p. 248°C (from EtOH) [23].

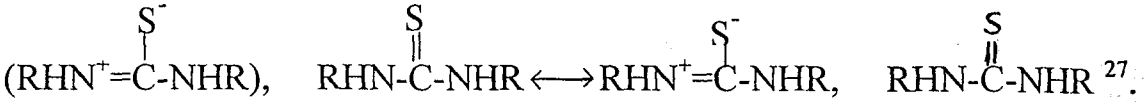
Thiocarbanilide can be condensed with an aldehydes, urea and phenols in the presence of a catalyst to produce an artificial resinpus substance [24]. The catalyst may be an acid, an alkali, or a thiocynate.

Derivatives of thioureas of ArNHCSNHAr type reacts with acids to give different products [25]. Sy-diphenylthiourea when heated with HCO_2H yielded $PhNH_2$, formanilide contaminated with a little $PhNH_2$ depending on the weight of the diphenylthiourea and period of the reaction. AcOH on heating 4hrs. gave AcNHPh, m.p. 114°C. Similarly $EtCO_2H$ gave propionoanilide, m.p. 105°C $PrCO_2H$ gave butyranilide, but CO_2H gave valeranilide [25].

1.5 Chemical Analysis of Thiocarbanilide:

In the determination of dielectric polarization of thiocarbanilide, was found the dipole moment ($\mu \times 10^{18}$) of $CS(NHPh)_2$ is about 4.85. The dipole moment of C-S bond is greater than that of the C-O bond [26].

According to the high melting point of diphenylthiourea and its derivatives, its insolubility in non-polar solvents, its behaviour towards acids it was assumed to be having a zwitterion-formula (I), scheme 1, it was suggested to have a tautomeric equilibrium (II). Although latter the Zwitterion was abandoned in favour of the classical formula (III)



(I) (II) (III)

Scheme 1

Yet the dielectric behoviour of diphenylthiourea in aqueous solutions indicated the presence of some molecules of type (I). Diphenylthiourea has a dipolmoment of 4.9 D. With respect to the data obtained for the dipole moment and in terms of the "Zwitterion" theory. It was obvious that increasing substitution of the diphenylthiourea molecule prevented increasingly the electron transfer from the nitrogen to the sulfur atom[27] .According to the infrared spectroscopic and dielectric measurements on the thio- compounds, there was found that the ratio of the frequencies νCS/νCO = 1.5 the ratio varied over the range 1.14-1.45 for thiourea and N, N'-dimethylthiocarbanilide[28]. The peptide and thiopeptide groups [NH(C:X)] where X is either O or S, are distinguished in the range 3-15μ by 5 characteristic bands; 3 denote NH valence oscillations near 3400 cm^{-1}, NH oscillations near 700-800 cm^{-1},

deformed out of their planes, and C:X valence oscillations near 1660-1100 cm^{-1}. The other bands indicate the amide –II (-CSNH-) near 1550 cm^{-1} [28].

It was supposed that the amount of C:S compounds was about 0.5 debye greater than for the C:O compounds, but actually it varied between zero and 2 debye, owing to the nature of the groups attached to the C:X groups [28].

According to the IR spectra of CuCl. 2L (L=diphenylthiourea), was suggested that Cu(I) is coordinated through S in all cases, except that of allythiourea [29].

$SC(NHPh)_2$ showed tautomeric equilibrium with its thioenol form, HSC(:NPh)NHPh , in C_5H_5N solution the spectrum of $SC(NHPh)_2$ showed no SH frequency in C_5H_5N solution the C:N and SH frequency were both evident [30].

The UV spectrum of a number of arylthiourea have been measured. The band in the spectra of arylthioureas is assigned the $\pi \longrightarrow \pi^*$ thiourea transition, some what modified by Phenyl substitution [30].

In a series of sym-disubstituted (mostly) P-P')N,N'-diphenylthioureas a linear relation is observed between the band frequency and Hammett substituent constants. Symmetry and steric effects are considered to be important in a number of the arylthioureas [29].

Specctroscopic studies on n-Donar+б-Acceptor Systems : Thiocarbanilides [31].

The donar-acceptor interaction of thiocarbanilide with halogen have been investigated in detail employing electronic and infra-red spectroscopy[31].

Various correlation of the spectroscopic and thermodynamic data have been presented of the various donar acceptor system, the n-donar-б-acceptor complexes were associated with high thermodynamic stability.

. Sulphur would be expected to be a good donor atom since its ionization potential is relatively small.

Further the $n \longrightarrow \pi^*$ transitions of thiocarbonyl compounds occur at much longer wavelength than the corresponding carbonyl compounds [31].

Spectroscopy and thermodynamics of charge transfer complexes of substituted thiocarbanilide with halogens and phenols have been investigated.

Detailed studies on the infra red spectra of thioamides, thioureas and related systems, have shown that in all these systems the C=S stretching vibration is not localized and there is considerable mixing of vibrations. Such a study would throw some light on the structure of the donar acceptor complexes.

For thiocarbanilides, no unique charge-transfer band was observed as there was considerable overlap of the donar and charge transfer absorption.

The equilibrium constants were therefore evaluated by measuring the absorbance of the thiocarbonilide +iodine solution at the three wavelengths in the region 400-420 mμ where the blue- shifted iodine band was found to occur as a shoulder on the main band around 312 mμ. Fairly good correspondence was obtained between the values of K calculated at the three wavelengths. From the charge-transfer complexes a few thiocarbanilides with iodine have been investigated that the equilibrium constants are fairly high and increase with increasing electron donating ability of the substituents on the benzene ring.

Thus the equilibrium constant is highest for P, P'-dimethoxy thiocarbanilide and lowest for P, P'-dibromothiocarbanilide.

The correspondence between the charge transfer and $n \longrightarrow \pi^*$ transition energies as well as the direction of substituent effects on the charge-transfer equilibria indicate that sulphur is probably the donar atom in these systems.

Unit cell dimensions and space groups of sym-diphenylthiourea [32]:

A preliminary X-Ray examination of sym-diphenylthiourea has been carried out to study the crystal and molecular structures of the derivatives

of thiourea [32]. From the examination of the ultraviolet absorption spectra of the substituted ureas, Picard and McKay [33] pointed out that some double bond character exists between nitrogen of thiourea and the phenyl group [33]. Since thiourea is known to have planner structures, one can predict that their substituted compound should have a similar configuration having a molecular symmetry identical with that of the parent molecules [32].

The result of the preliminary work on sym-diphenylthiourea shows that this compound has the some molecular symmetry as thiourea [32].

The crystals obtained by recrystallization from benzene are thin plates on (001) outlined by (100) and (010) [32].

Ascending paper chromatography is suitable for detection and separation of diphenylthiourea in aqueous or anhydrous solvents systems.

The best separation, development of chromatogram within hour, was obtained by using cyclohexane as the mobile phase, the development was much slower. The limit of detection was 0.59 μg [34].

The crystal structure determination of the little compound 1,3-bis (2-chlorophenyl) thiourea at 173 K is reported [35].

There are two molecules in the asymmetric unit connected by N-H···· S hydrogen bonds and a short Cl····Cl contact [35]. The molecules exists as a dimers and the crystal lattice consists of two-dimensional parallel layers of these dimers connected by C-H····Cl hydrogen bonds [35].

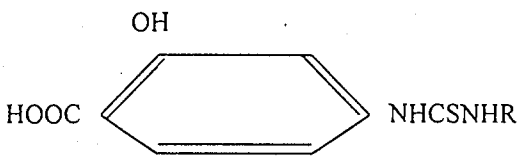
1.6. Biological properties of thiocarbanilide:

1.6.1. Antituberculous activity:

Many thiocarbanilides have been tested for antitubercular activity.

A number of thiocarbanilide of P-aminosalicylic acid in vitro tests were found to be equal to or more active than the acid itself [1].

Maximum activity in compounds of type



was achieved when R was aromatic. If R was aliphatic or if O-or m-aminosalicylic acid was used instead of p-aminosalicylic acid, the activity dropped or completely disappeared[1]. The compound 4,3-(HOOC)(HO)C_6H_3NHCSNHC_6H_5 was found to prolong life in animal studies but, although the disease was arrested, it did not produce a complete cure, In clinical tests there was no evidence of development of resistance to this compound [2].

4,4'-diethoxythiocarbanilide was found to posses high antitubercular activity in the mice infected with bacillus H_{37}Rv [1].

Hence over three hundred thiocarbanilides were made and tested. These compounds were tested in vitro against *M. tuberculosis* and in vivo in experimentally infected mice.

Almost one third of these compounds, the majority of which were 1,3-di (4-substituted phenyl) thioureas, showed significant activity in the in vivo studies in mice [1].

Eight of the more active thiocarbanilides were subjected to the tests in guinea pigs [1], and seven of these showed suppressive effects. Two of the seven thiocarbanilides, 4-ethoxy-4-isobutoxythiocarbanilide and 4-n-butoxy-4-dimethylaminothiocarbanilide, exceeded the activities of P-amino salicylic acid and streptomycin and approached that of isoniazid [1]. Combinations with streptomycin and isoniazid gave enhanced effects.

From these data certain specific structural requirements were observed for the antituberculous activity of thiocarbanilides of the following structure [1].

(a) Shortening of the 4-substituent to CH_3O- destroys the activity.

(b) Lengthening of the chain in the 4-substituent increases the activity to a maximum at three to four carbon atoms. Further increase in chain length causes a decrease in activity until it completely disappears at R=$C_8H_{17}O$-.

(c) Replacement of the alkoxy group by an alkyl group of the same length gives similar activity.

(d) Branching of the alkyl at the carbon atom adjoining the ring leads to the loss of activity.

(e) If one of the 4-alkoxy groups is replaced by a halogen or dialkylamino substituent, activity is retained.

(f) Replacement of both alkoxy groups by halogen or dialkylamino groups causes total loss of activity.

(g) That the 4-substituent is necessary in both rings is shown by the fact that replacement of one alkoxy group by hydrogen causes loss of activity. Further more, the 2- and 3 position isomers are inactive.

(h) A second substituent in the ring destroys the activity, as dose an additional substitient on the ureido nitrogen.

(i) The thiocarbanilide moiety is necessary, since corresponding carbanilides, guanidines, guanylthiourea, dithiobiuretes, and cyclohexyl- substituted thioureas are inactive [1].

Buun-Hoi and Xuong [1], who prepared a number of thiocarbanilides for antituberculosis studies, believe that the metal-chelating property of thiocarbanilide and a favuorable partition coefficient for the molecule between aqueous and fatty phases are instrumental in their activity.

1.6.2 Antibacterial properties:

It is interesting to note that some of the 1,3-di(substituted phenyl) thioureas which possessed high antituberculous activity also had significant activity against several species of actinomyces and fungi[1].

1.6.3 Antiviral properties:

Experimental chemotherapy of influenza with 1,3-diarylthiourea and analogous sulphur–containing derivatives was made. Certain of the 1, 3-diarylthiourea compounds showed significant activity against type-A-influenza virus [36]. For the S-containing compounds there appeared to be no relation between antiviral and tuberculostatic properties.

1.6.4 Metabolic activity:

The metabolic sequence of substituted thiocarbanilides may involve the release of H_2S which could block Fe and Cu enzymes [37]. The main metabolites of diphenylthiourea are the glucuronide of 4-hydroxy- and 4, 4' dihydroxydiphenlyl thioureas [37].

It was suggested that toxicity of thiocarbanilide is related to metabolic loss of S.

1.6.5 Insecticidal properties:

Some thiocarbanilides have been found to be useful as insecticides. Substituted thiocarbanilides were tested for toxicity against house fly larvae. The more active one is thiocarbanilide itself, known compounds tested are N, N'-diphenylthiourea, N, N'-bis (P-chlorophenyl) thiourea and N, N'-bis (P. methoxyphenyl) thiourea [38].

1.6.6 Rodenticidal activity:

Thiocarbanilides are much more toxic to rats than it is to cats [39].

These agents cause early depression, later the excitability of higher functions is increased leading to convulsion, coma and death. Compound of mild toxicity is 1,3-bis (2,4,6 trichlorophenyl) thiourea [39].

1.7 Objective of the study:

Preparation of organometallic compounds from thiocarbanilides and substituted thiocarbanilides using manganese(II) chloride, and investigating of these compounds with spectroscopic means to prevail the mechanism of the reaction.

CHAPTER TWO

EXPERIMENTAL

2. Experimental:

Melting points were determined on melting point apparatus. IR spectra were recorded on a Perkin -Elmer Model 1330 infrared spectrophotometer, and UV spectra were recorded on UV/VIS spectrophotometer model 55OS. H' nmr spectra and mass spectra were obtained by Lash Miller Chemical Labs. University of Toronto, Ontario, Canada.

2.1 Preparation of thiocarbanilide (sym-diphenylthiourea) and substituted thiocarbanilides

(1) Thiocarbanilide [40]: $C_6H_5NHCSNHC_6H_5$

In 250 ml round-bottomed flask provided with an efficient double surface condenser, was placed aniline (9.75c.c.), carbon disulphide (10c.c.) and absolute ethyl alcohol (15.87c.c.). The apparatus was set up in the fume cupboard to absorb the hydrogen sulphide which was evolved. The mixture was heated upon an electrically- heated water bath for more than eight hours until the contents of the flask solidified. After completion of the reaction, the condenser was arranged for downward distillation and the excess of carbon disulphide and alcohol were removed. The residue in the

flask was shaken with excess of dilute hydrochloric acid (1:10) to remove any aniline present, then was filtered, washed with distilled water and drained well. The product was dried in the steam oven. The yield was 70.5%. Recrystallized from rectified spirit. Pure sym-diphenylthiourea was separated in colour-less leaflets crystals, (m.p. 153°C, Lit. 154°C), almost insoluble in water, completely soluble in hot alcohol, hot ether and benzene. ν max.cm^{-1} (KBr) 3200 (N-H stretching), 3000 (aryl C-H stretching), 1590, 1530 and 1500 (aromatic, C=C), 1070 (C=S stretching), 1450 (-CS-NH-amide II), 1340, 1200 (-CSNH- amide I), 930, 760 and 690 (aromatic C=CH); λ max. (Dimethoxy ethane) 285nm (ε = 22800).

(II) 2:2'- dimethylthiocarbanilide [41] :(di-o-tolythiourea):

To a mixture of orthotoluidine (10.7 gm) in carbon disulphide (9.5 c.c.) which was placed in a 250 c.c. round bottom flask equipped with reflux condenser, was added slowly a solution of sodium hydroxide (40%, 10c.c.). The mixture was stirred magnetically and refluxed for an hour. A colourless solid separated, water, 20 c.c., was added, then it was filtered, washed with water and dried. The product was recrystallized from ethanol, (m.p. 163C°, Lit. 163C°), the yield was 93.7%, solube in AcOH, benzene and hot ethanol, insoluble in Et_2O.

νmax. cm^{-1} (KBr) 3320 (N-H stretching), 3140 (aryl C-H stretching), 2950 (CH_3), 1500 (aromatic C=C), 1330 (-CS-NH- amide II), 1260, 1230 and 1210 (-CSNH- amide I), 110 (C=S stretching), 920, 760, 740 and 720 (aromatic C=CH), λmax. (Dimethoxyethane) 286 nm (ε=11490).

(III) 3:3-Dimethylthiocarbanilide[41] : (di-m-tolythiourea):

This compound was obtained in a 70.3% yield as in the above method. It was recrystallized from benzene in colourless prism, (m.p. 111C°, Lit. 113C°), soluble in hot ethanol, hot acetone, moderately soluble in hot water. νmax. cm^{-1} (KBr) 3360 (N-H stretching), 3180 (aryl C-H stretching), 2960 (CH_3), 1585, 1510 (aromatic C=C), 1350 (-CS-NH-amide II), 1285, 1220 and 1160 (-CSNH-amide I), 1080 (C=S stretching), 780, 720 and 680 (C=CH aromatic); λ max. (DME) 281nm (ε=18000).

(VI) 4:4′- dimethylthiocarbanilide [41] : (di-p- tolythiourea):

The compound was obtained in a 77.4% as faint- yellow granulated crystals from ethanol, (m.p. 176C° Lit. 177C°) according to the pervious preparations. It is moderately soluble in ethanol, insoluble in water. ν max. cm^{-1} (KBr) 3160 (N-H stretching), 3040 (aryl C-H), 2960 (CH_3), 1590, 1550, 1480 and 1400 (C=C), 1320 (-CS-NH-amide II), 1280, 1240 and

1180 (-CSNH-amide I), 1140, 1020 (C=S stretching), 860, 800 and 700 (C=CH aromatic); λ max. (DME) 294 nm (ε =12367).

(V)2:2'-di-chlorothiocarbanilide[10]:(1:3-di-(ortho-chlorophenyl) thiourea:

A mixture of ortho-choroaniline (0.02 mole), carbon disulphide (30.0 c.c.), pyridine (0.04 mole) and iodine (0.01 mole) were placed in a round–bottomed flask connected by a ground-glass joint to a reflux condenser and was heated to gentle boiling as long as hydrogen sulphide was evolved, the reaction was completed when the colour of iodine had disappeared and the pyridinum iodide had completely precipitated. Then the mixture was steam–distilled until all traces of carbon disulphide and pyridine were gone. The pyridinium iodide was easily removed by washing with water.

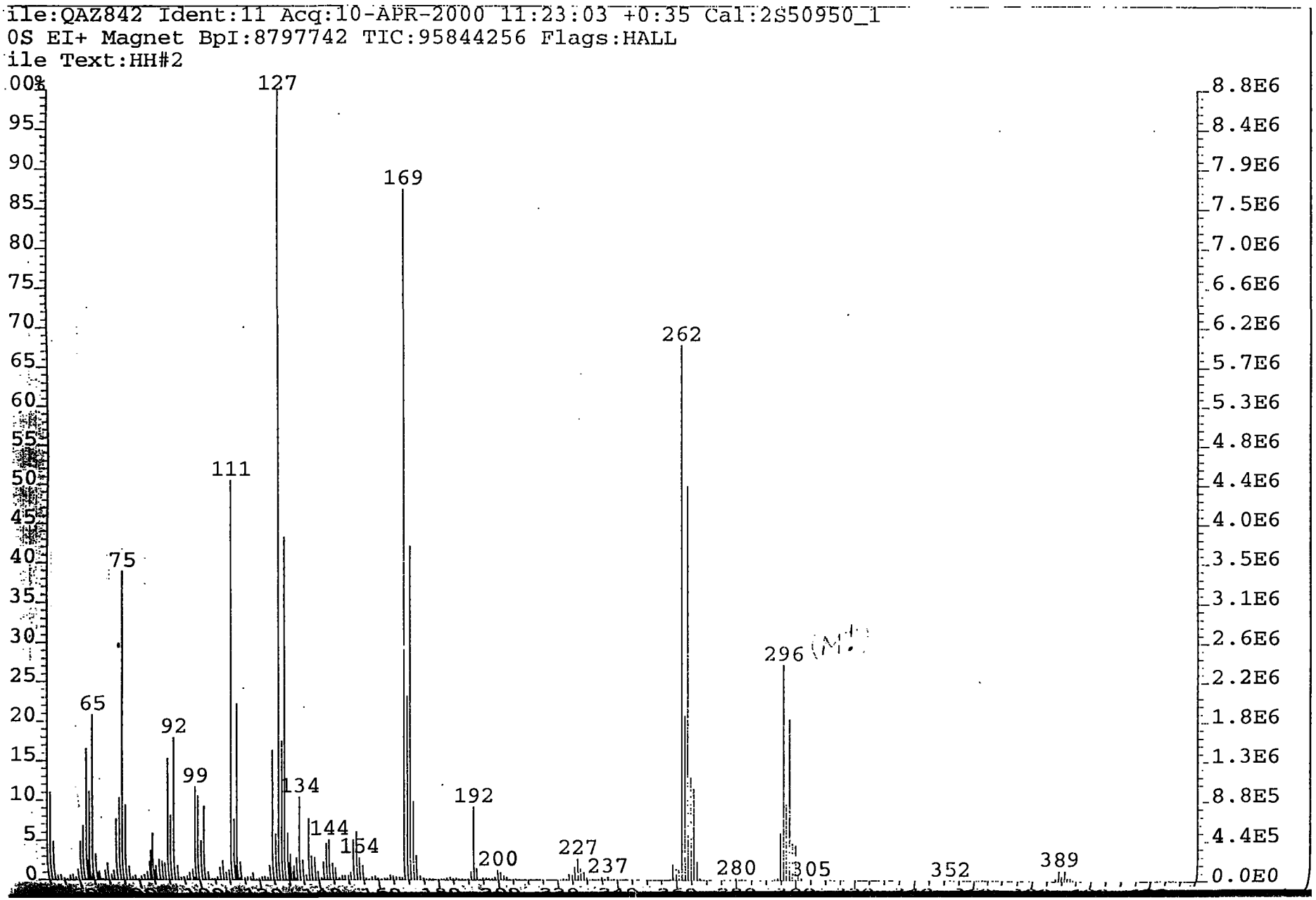
The yield was 76.0%. The product was recrystallized from ethanol in yellow felted needle like crystals. (m.p. 129°-130°C, Lit. 131°C). ν max. cm^{-1} (KBr) 3360 (N-H stretching), 3100,2940 (aryl C-H), 1590, 1520 and 1440 (C=C), 1340 (-CS-NH- amide II), 1280, 1240 and 1200 (-CSNH – amide I), 1060 (C=S stretching), 750, 720 (C=CH aromatic), λ max. (DME) 287 nm (ε =10846).

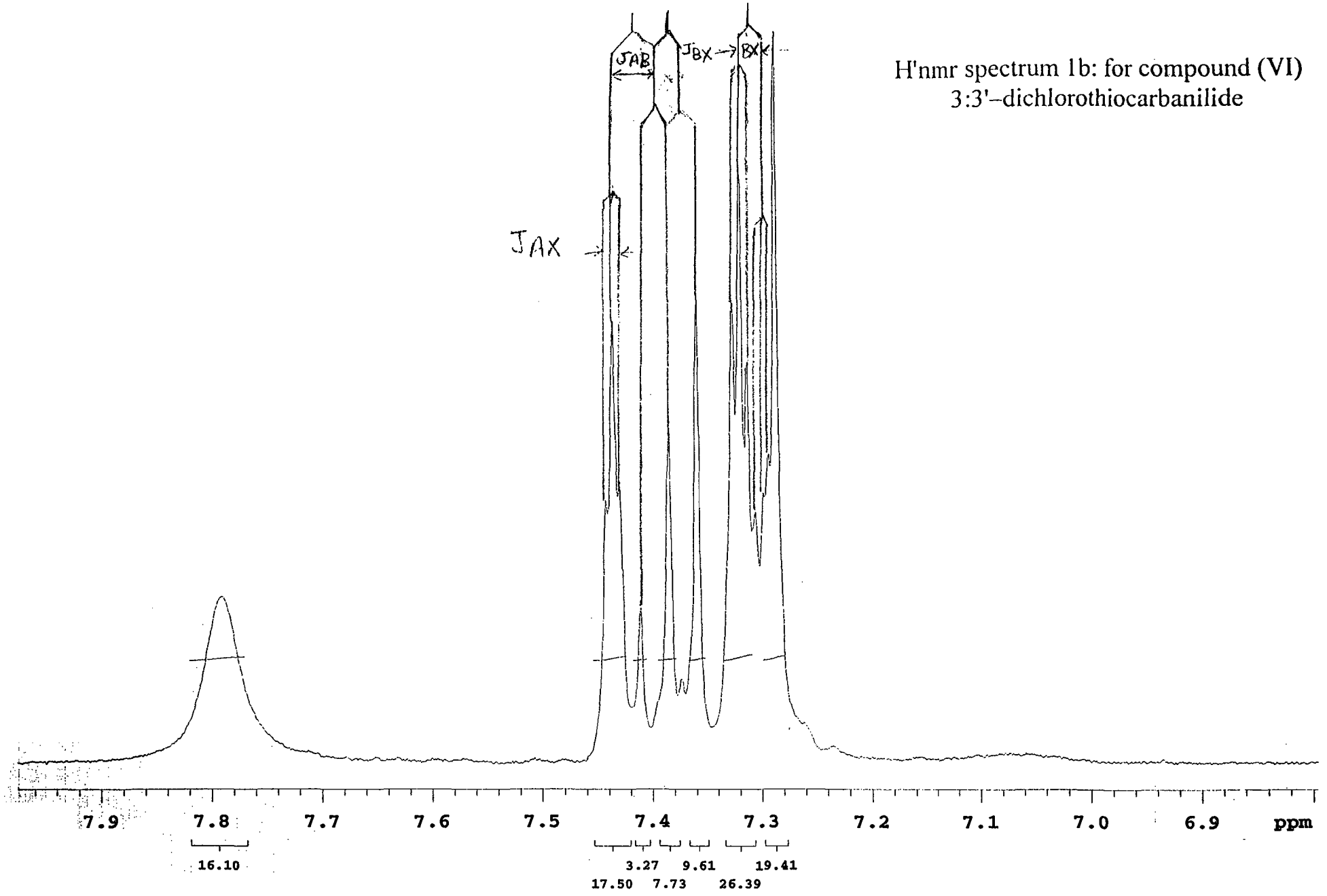
(VI)3:3'–dichlorothiocorbanilide[10]:(1:3-di-(meta-chlorophenyl) thiourea:

According to the previous methods the compound was obtained in a 74.0% yield. It was recrystallized from benzene in white needle like crystals, (m.p. 121°C- 122°C Lit. 120°C), easily soluble in alcohol, insoluble in water. νmax. cm^{-1} (KBr) 3360 (N-H stretching), 3190,3020 (aryl C-H), 1585,1330, 1470 and 1420 (C=C), 1305 (-CS- NH- amide II), 1250 (-CSNH- amide I), 1080 (C=S stretching), 970,860 and 770 (C=CH aromatic), 680 (C-Cl), λ max. (DME) 283 nm (ε= 15200); m/z 296 (27%) (figure 1).

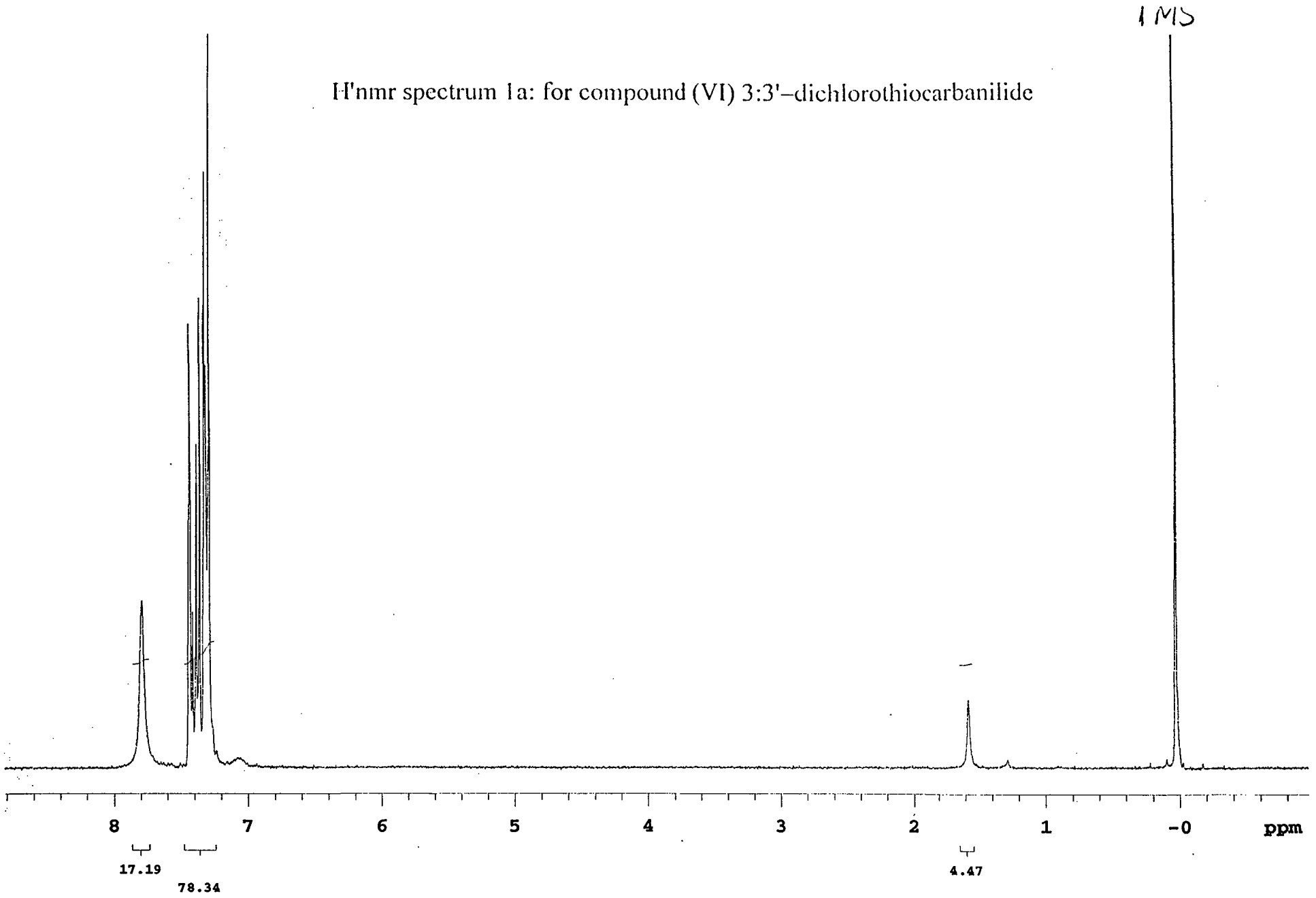
The H´nmr of this compound (spectrum 1a and 1b) was characterized by the splitting of nitrogen proton absorption into singlet at δ7.78ppm, the signals at δ7.28-7.44 ppm were splitting of the protons of the substituted phenyl, which was coupled into ABX system, in which δA = 7.4426 ppm,δB = 7.367ppm and δ X = 7.308ppm; ^{J}AB = 10.0Hz, ^{J}AX = 1.87Hz and ^{J}BX = 6.25Hz. The singlet at δ 7.286ppm of the proton at ortho-position near to the meta-chlorine. According to the integration there was a single proton at δ 7.78ppm and four protons at δ 7.28- 7.44ppm.

Figure 1: Mass spectrum for compound (VI) 3:3'–dichlorothiocarbanilide





H'nmr spectrum 1b: for compound (VI)
3:3'–dichlorothiocarbanilide



H'nmr spectrum 1a: for compound (VI) 3:3'–dichlorothiocarbanilide

(VII)4:4′-di-bromothiocarbanilide[10]:(1:3-di-(para-bromophenyl) thiourea:

This compound was obtained in a 77% yield as in the two previous methods. It was recrystallized from alcohol in bright needle crystals, (m.p. 188°C, Lit, 189°C); ν max. cm^{-1} (KBr) 3200 (N-H stretching) 3000 (aryl C-H), 1580, 1530 and 1480 (C=C), 1390, (-CS- NH- amide II), 1300, 1280 and 1220 (-CSNH- amide I), 1070 (C=S stretching), 810 (C=CH aromatic) 710 (C-Br); λmax. (DME) 291 nm (ε =17365).

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

(VIII) 3:3′-dichlorothiocarbanilide.$MnCl_2$ complex [16]:

Manganese II chloride (0.66 gm) was dissolved in distilled water (20 c.c.), and was added dropwise to a suspension of 3:3′-dichlorothiocarbanilide (1.0gm) 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); ν max. 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), λ max. (DME) 325nm (ε =748); m/z 717 (49%), m/z less Cl 682 (58%), m/z less 2Cls=647 (70%), (Figures 2, 3 and 4); H´nmr of this compound is blurred (spectrum 2, 3 and 4).

(IX) 3:3´- dimethylthiocarbanilide. $MnCl_2$ complex[16]:

ManganeseII chloride (o.38gm) was dissolved in distilled water (10. c.c.), and was added dropwise to a suspension of 3:3´-dimethylthiocarbanilide (0.50gm) 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). ν max. cm^{-1} (KBr) 3360 (N-H stretching), 3160 (aryl C-H), 2960 (CH_3),

Figure 2: calculated distribution for molecular weight for compound (VIII)
(3:3'–dichlorothiocarbanilide)$_2$.Manganese (II) chloride

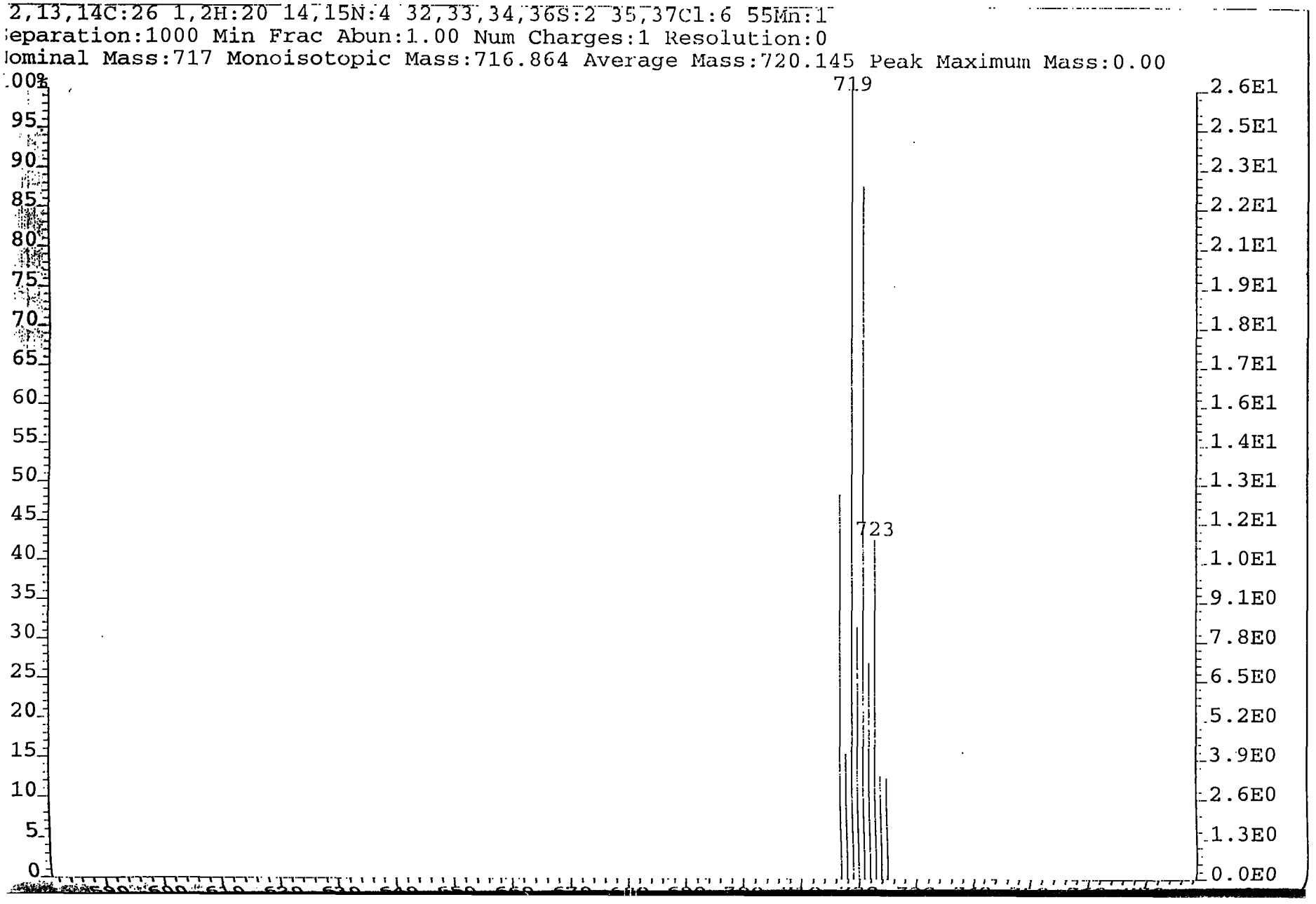
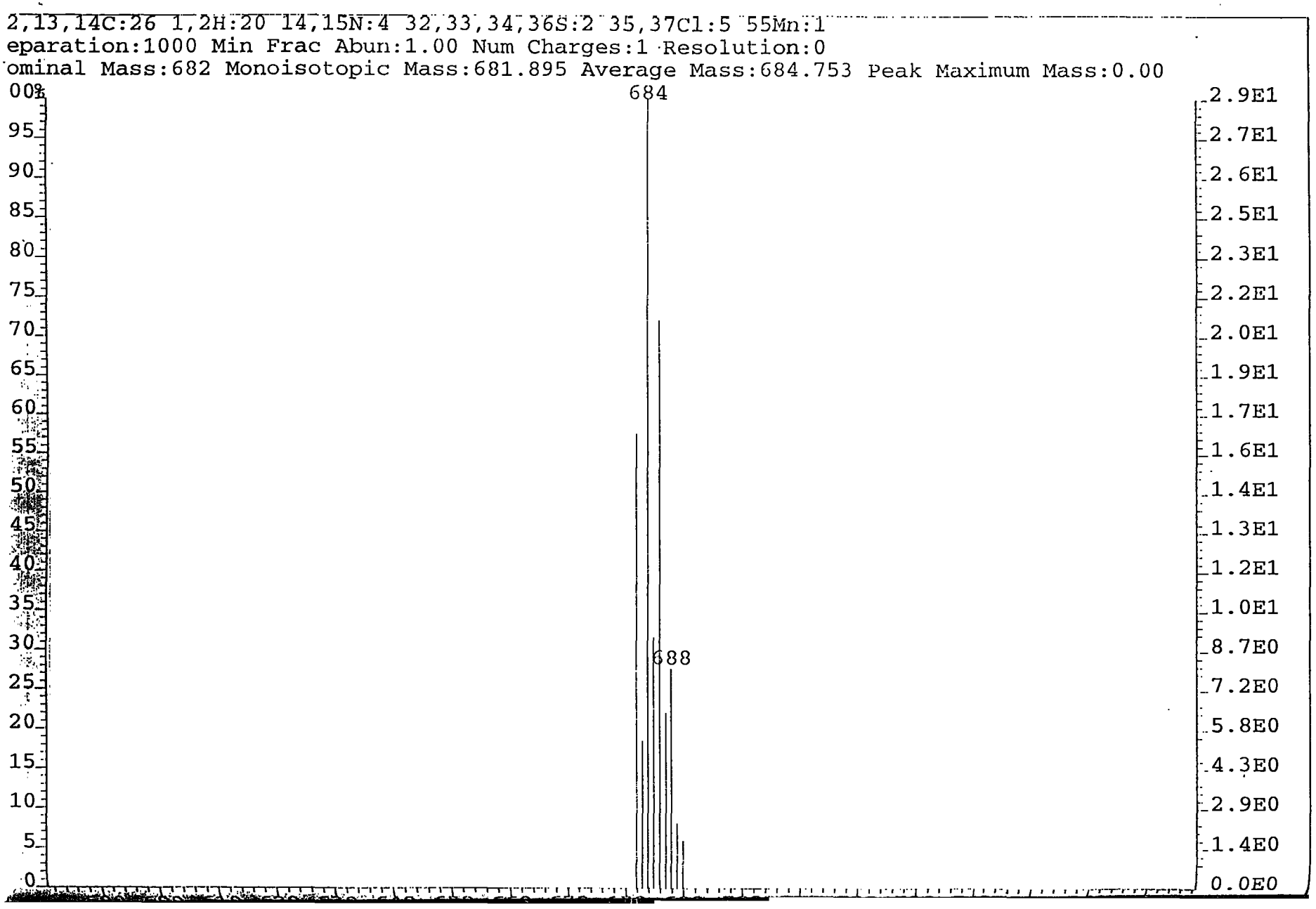
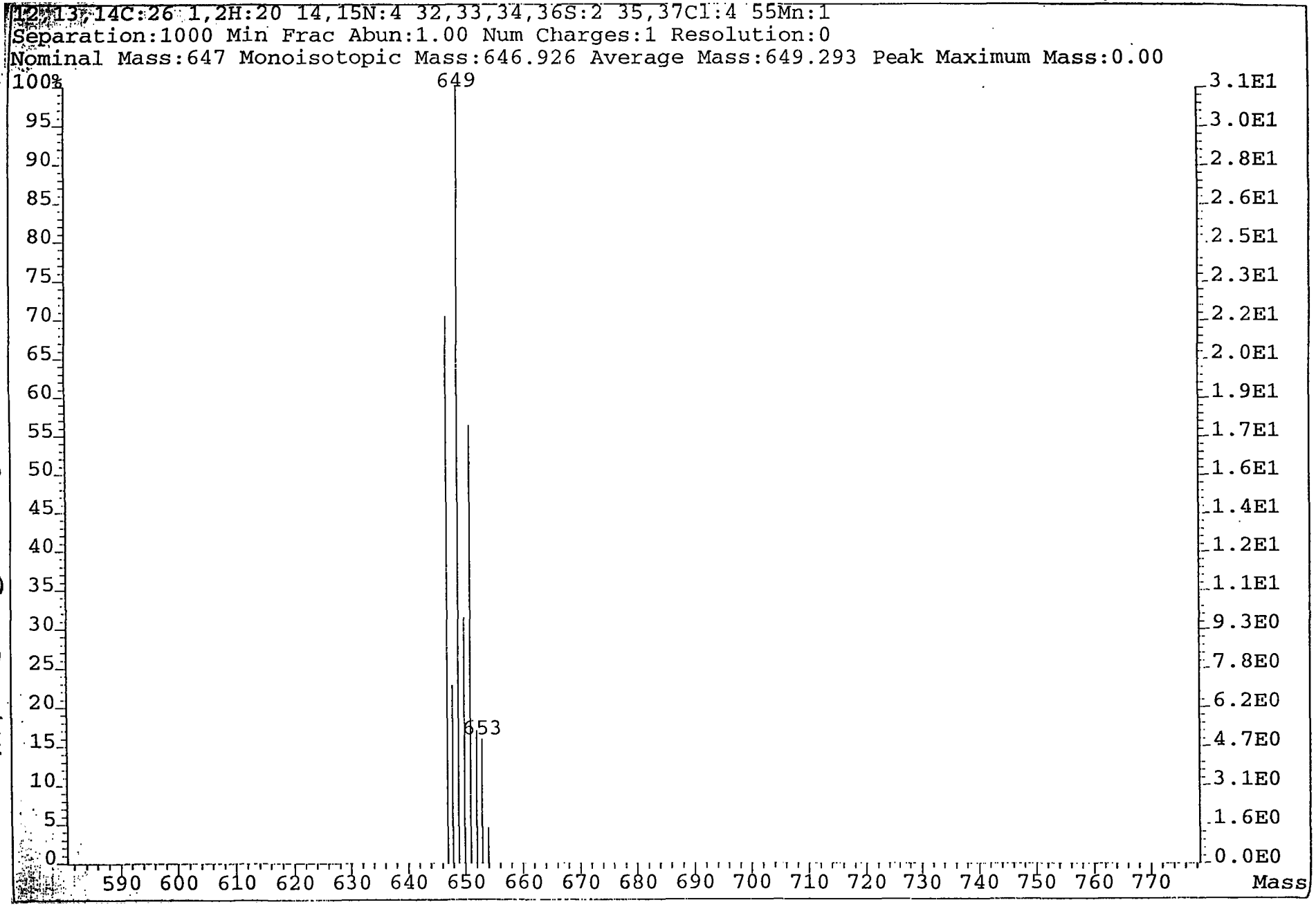
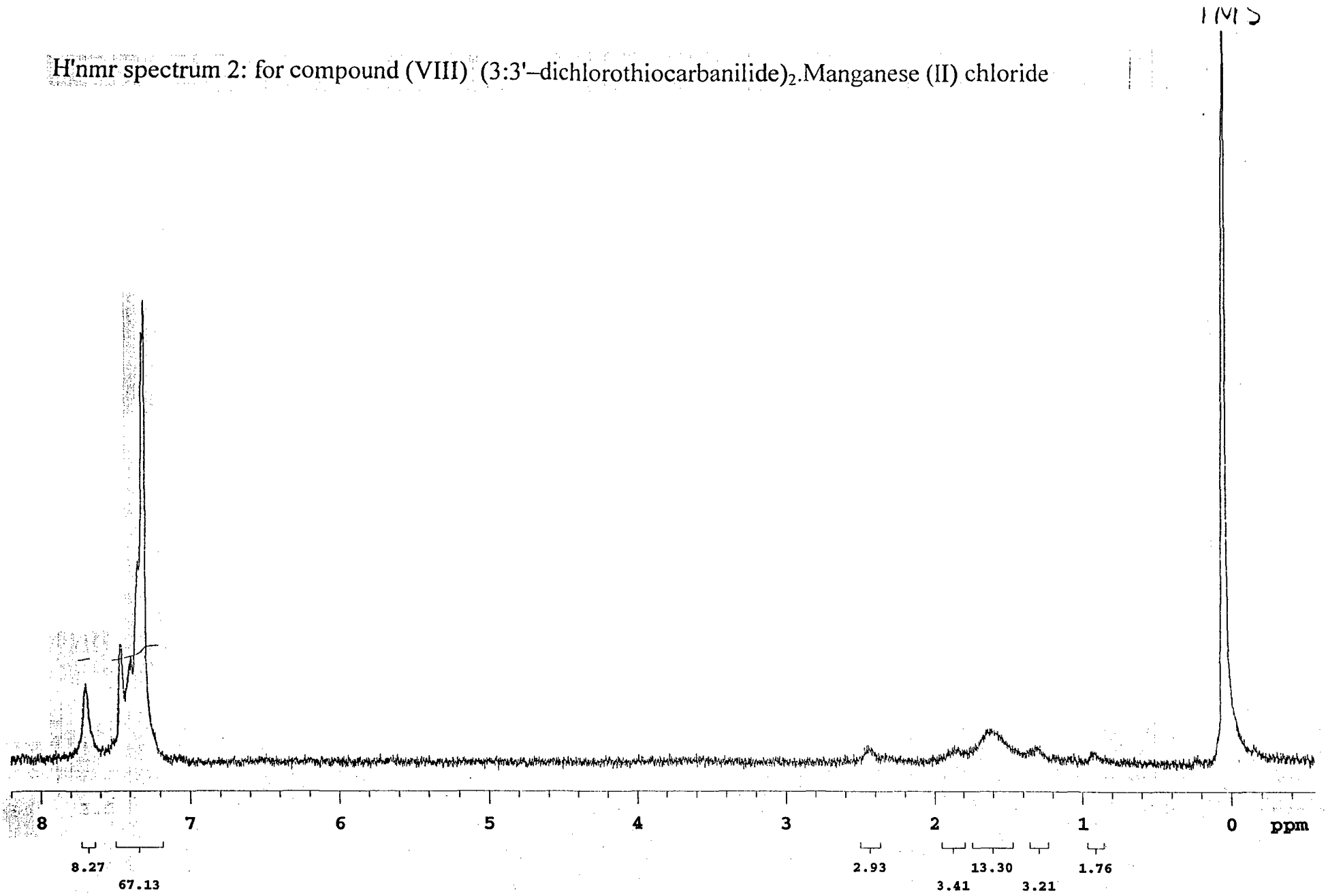


Figure 3: m/z less Cl for compound (VIII) (3:3'–dichlorothiocarbanilide)$_2$.Manganese (II) chloride

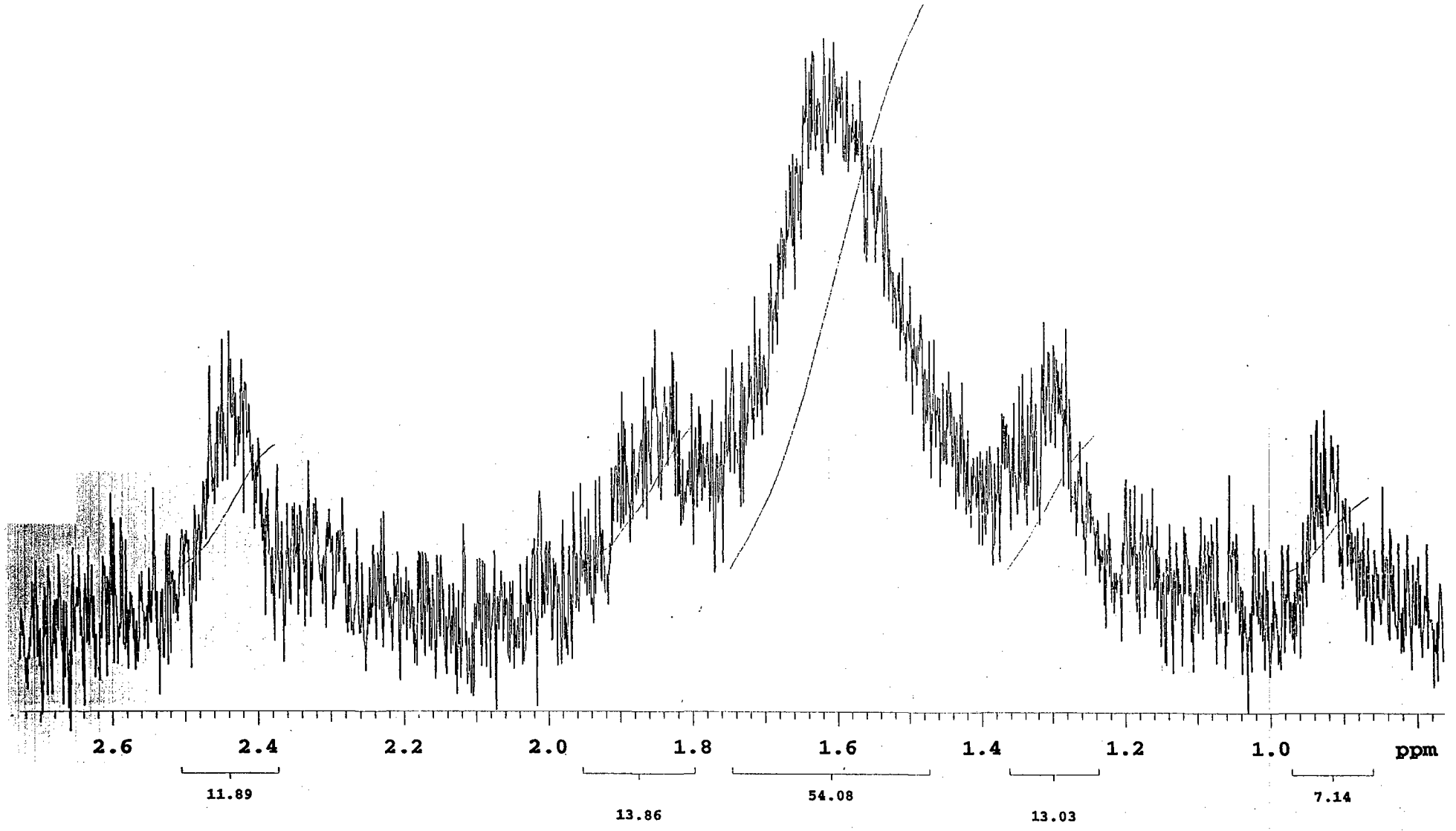



12,13,14C:26 1,2H:20 14,15N:4 32,33,34,36S:2 35,37Cl:4 55Mn:1
Separation:1000 Min Frac Abun:1.00 Num Charges:1 Resolution:0
Nominal Mass:647 Monoisotopic Mass:646.926 Average Mass:649.293 Peak Maximum Mass:0.00
RELATIVE ABUNDANCE
100%
649
653
3.1E1
3.0E1
2.8E1
2.6E1
2.5E1
2.3E1
2.2E1
2.0E1
1.9E1
1.7E1
1.6E1
1.4E1
1.2E1
1.1E1
9.3E0
7.8E0
6.2E0
4.7E0
3.1E0
1.6E0
0.0E0
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
590 600 610 620 630 640 650 660 670 680 690 700 710 720 730 740 750 760 770
Mass

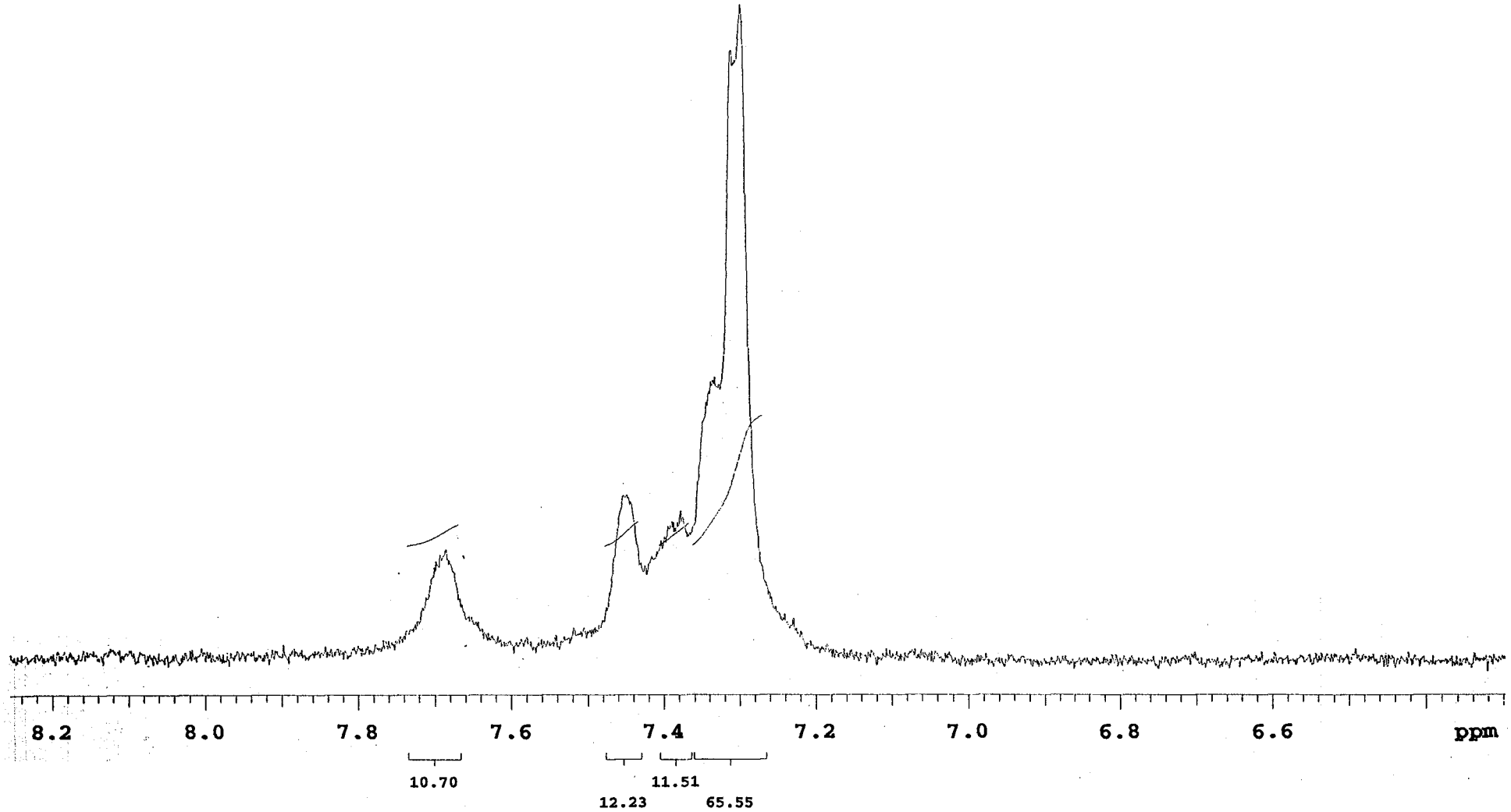
H'nmr spectrum 2: for compound (VIII) (3:3'–dichlorothiocarbanilide)$_2$.Manganese (II) chloride



H'nmr spectrum 3: for compound (VIII) (3:3'–dichlorothiocarbanilide)$_2$.Manganese (II) chloride



H'nmr spectrum 4: for compound (VIII) (3:3'–dichlorothiocarbanilide)$_2$.Manganese (II) chloride



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);λ max. (DME) 334nm (ε =924).

(X) 2:2′-dimethylthiocarbanilide .$MnCl_2$ Complex[16]:

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. ν max. cm^{-1} (KBr) 3320 (N-H stretching), 3140 (aryl C-H), 2950 (CH_3), 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);λ max (DME) 336nm (ε =805).

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 Lassiagne'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.

2.4 Estimation of nitrogen[42]:

Kjeldahl method:

Di-meta-chloro-thiocarbanilide.$MnCl_2$ (0.20gm) was placed in a special long-necked "Kjldahl flask". Concentrated sulphuric acid (5c.c.) a little potassium sulphate and copper sulphate as catalyst were added to the flask. The flask was loosely stoppered by a glass bulb, and was heated gently in an inclined position. The heating was continued for two hours

until the clear solution was obtained. At this point all the nitrogen in the substance was converted to ammonium sulphate. The Kjeldahl flask was then cooled and its contents were diluted with some distilled water, and then carefully was transferred into another conical flask. Sodium hydroxide solution (20c.c. 40%)was poured down the side of the flask. Then the flask was connected to distilling apparatus. The apparatus was heated and the liberated ammonia was distilled into boric acid (10c.c.2%). The distillation was continued about 20 minutes until the liberation of ammonia had stopped.

Then the distillate was titrated against 0.2 M HCl using cressol green as indicator.

This method was repeated three times. The volumes of the HCl were found as follows 5.70 c.c., 5.65. c.c. and 5.60 c.c. The average volume was 5.65 c.c.

$$\text{Percentage of nitrogen} = \frac{(V-V_1) \times 14 \times 100 \times M}{1000 \times X}$$

where V = volume of the acid used up

V_1= Blank

M= The molarity of the acid used

X= Weight of sample (substance Kjeldallized)

Then:

$$\%N_2 = \frac{(5.65\text{-}0.1)\ X14X0.2X100}{0.2\ X\ 1000}$$

$$\%N_2 = 7.77$$

The calculated is about 7.79%

2.5 Determination of Molecular Weight [43]:

Rast's camphor method:

A small clean weighed tube was supported in a hole bored in a cork so that it stood properly on the pan of a balance.

The tube was weighted. Di-meta- chlorothiocarbanilide- $MnCl_2$ (50 mg) was introduced into the tube and it was weighted again. Then resublimed camphor (500mg) was added and the tube was weighted again.

Then the tube was stoppered lossely and the contents were melted by placing it in an oil bath previously heated to about 180 c°.The liquid was stirred . It was allowed to cool, the solid was transferred to a clean watch glass where it was ground. Some of the powder was introduced into a thin capillary tube of which the closed end was carefully rounded, the solid was pressed down into the closed end with aid of a closed capillary tube of smaller diameter. The melting point of the mixture was determined by

using a 100-200 thermometer gradulated in 0.2 ,this methed was repeated three times. The melting point of the mixture was determined .Original camphor m.p. 174.2 c°.

The difference in melting points gave the depression of the melting point of camphor caused by the addition of the compound.

The molecular weight M can then be calculated from the formula:

$$M = \frac{KXWX\ 1000}{DT\ X\ W}$$

Where K is the moleculor depression constant of camphor (39.7)

W is the weight of the compound.

W is the weight of the campher

And DT is the depression of the melting point.

The method was repeated three times, the melting points of the mixture were 168.7C°. 168.7C° and 168.6 C°. Then DT is 5.5 C°, 5.5 C° and 5.6 C°, and the main value of DT is 5.533 C°.

Then the moleculer weight is

$$\frac{39.7\ X\ 50\ X\ 1000}{5.533\ X\ 500} = 717.5$$

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 Reaction of unsubstituted thiocarbanilide (I) with $MnCl_2$ in different media:

3.1.1 The reaction between compound (I) 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 [9], desulfurization of thiocarbanilide took place by $Cu(OH)_2$ and $Pb(OH)_2$ forming dark colour of metal sulphide and yellow oil which might be isothiocynate (PhNCS).

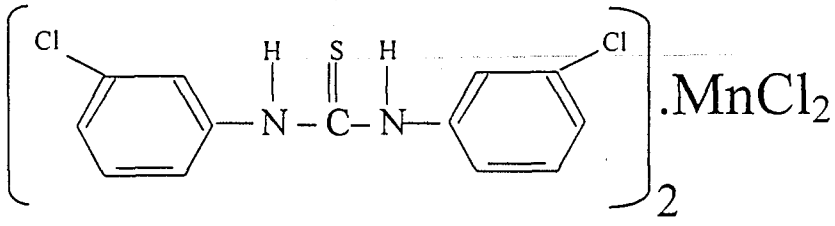
3.1.2 The reaction between compound (I) and manganese (II) chloride in aqueous medium acidified with conc. HCl, led to the liberation of hydrogen sulphide, and formation of white precipitate, no sulphur was present in the precipitate according to the lassiange's test. Literature review[11] explained that thiocarbanilide was easily oxidized in acidic solution by various reagents e.g. $KMnO_4$, KOBr, 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 (I) and manganese (II)chloride.

3.2 Reaction of substituted thiocarbanilide , compounds (VI), (III) and (II) with manganese (II) chloride:

3.2.1 Compound (VI), (III) and (II) were oxidized by manganese(II) chloride in aqueous acidic media. In each case the reaction gave the manganese(II) chloride complexes (VIII) "63%", (IX) "57.6%" and (X) "53%" respectively, which were coloured, decomposed by hot solutions, soluble in most organic solvents, insoluble in distilled water. The yields were fairly good, yet complex (VIII) gave the higher yield. In which case the reaction proceeded with formation of a gray green complex, that was found to give an m/z (717), m/z less Cl (682) and m/z less 2 Cls (647) (Figure 2, 3 and 4)

The molecular weight of 3:3'-dichlorothiocarbanilide.$MnCl_2$ (complex {VIII}) was found to be (717) by Rast's Camphor method and mass spectroscopy (Figure 2), the nitrogen content gave 7.77%, from this the molecular formula of the complex is (3:3'dichlorothiocarbanilide)$_2$.$MnCl_2$



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 λ max of the substituted thiocarbanilide are in the range 281 – 295 nm (Table 3), and the ultraviolet spectra of the complexes are in the range 325 – 336 nm (Table 4). The absorption of λ max in the thiocarbanilide is the based on the conjugation of the benzene ring, and the lone pair of the nitrogen atom and the two pairs of the functional group C=S, the increase in the λ max is the an indication of the formation of the complexes on these two atoms (-N- or C=S), (Table 4).

The infrared spectra of the complexes showed a clear N-H stretching (Tables 6, 7 and 8), hence there was no manganese-nitrogen bond formed.

There was a slight shift in C=S stretching, consequently there may be a manganese – sulphur bond.

Table (3):

U. V. and visible spectra maxima for substituted thiocarbanilide :

Compound	Concentration in mole/dm3	λ max in nm	Absorbance	ε
Thiocarbanilide	0.00010	285	2.280	22800
S-Di-o-tolythiourea	0.00011	286	1.149	11490
S-Di-m-tolythiourea	0.00010	281	1.800	18000
S-Di-p-tolythiourea	0.00015	294	1.855	12367
S-Di-o-chlorothiocarbanilide	0.00013	287	1.410	10846
S-Di-m-chlorothiocarbanilide	0.00010	283	1.520	15200
S-Di-p-bromothiocarbanilide	0.000085	291	1.746	17365

Table (3):

U.V. and visible spectra maxima for complexes of substituted thiocarbanilide . $MnCl_2$:

Compound	Concentration in mole/dm3	λ max in nm	Absorbance	ε
S-Di-m-chlorothiocarbanilide.$MnCl_2$	0.00139	325	1.040	748
S-Di-m-tolythiourea.$MnCl_2$	0.00157	334	1.450	924
S-Di-o-tolythiourea.$MnCl_2$	0.00130	336	1.046	805

Table 5

General layout of IR spectra of thiocarbanilides and substituted thiocarbanilides

Type of vibration	**Observed frequencies in cm^{-1}**
N-H stretching	3360-3160
Aryl C-H stretching	3190-3000
C=C aromatic	1600-1400
CH3 stretching	2960-2950
-CS-NH-	1450-1350
-CSNH-	1340-1100
C=S stretching	1140-1060
C=CH aromatic	970-640
C-Br	710
C-Cl	680

Table 6

Layout of IR spectra of 3:3'-dichlorothiocarbanilide (VI) and 3:3'-dichlorothiocarbanilide.Manganese (II) chloride complex (VIII)

Type of vibration	Frequencies in cm^{-1}	
	Compound (VI)	Compound (VIII)
N-H stretching	3360	3360
Aryl C-H stretching	3190	3190
Aryl C-H stretching	3020	3020
C=C	1585	1580
C=C	1530	1530
C=C	1470	1470
C=C	1420	1420
-CS-NH-	1305	1300
-CSNH-	1250	1250
C=S	1080	1075
C=CH	970	960
C=CH	860	860
C=CH	770	770
C-Cl	680	670

Table 7

Layout of IR spectra of 3:3'-dimethylthiocarbanilide (III) and 3:3'-dimethylthiocarbanilide.Manganese (II) chloride complex (IX)

Type of vibration	Frequencies in cm^{-1}	
	Compound (III)	Compound (IX)
N-H stretching	3360	3360
Aryl C-H stretching	3180	3160
CH3 stretching	2960	2960
C=C	1585	1580
C=C	1510	1500
-CS-NH-	1350	1340
-CSNH-	1285	1280
-CSNH-	1220	1220
-CSNH-	1160	1160
C=S	1080	1080
C=CH	780	780
C=CH	720	720
C=CH	680	680

Table 8

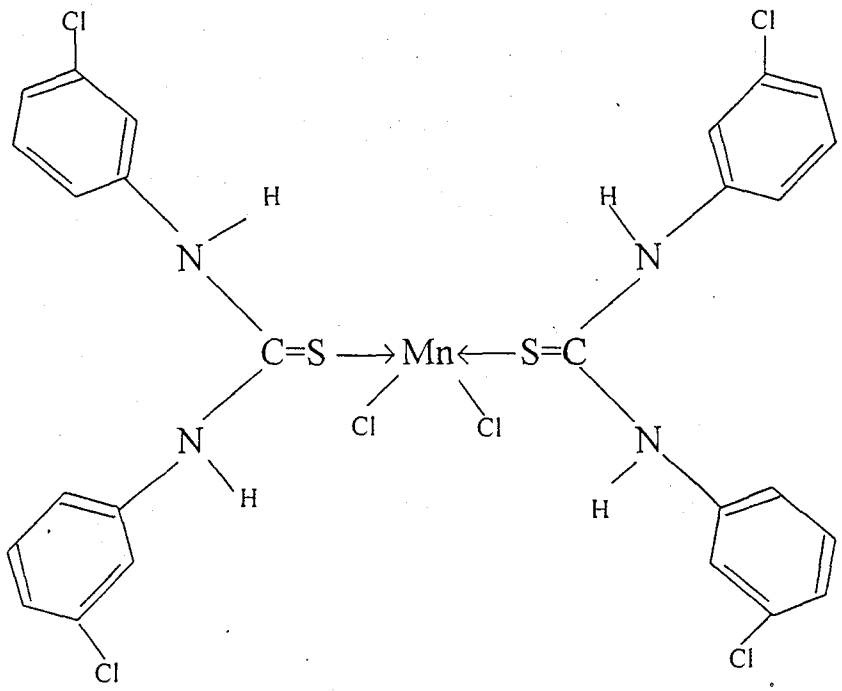
Layout of IR spectra of 2:2'-dimethylthiocarbanilide (II) and 3:3'-dimethylthiocarbanilide.Manganese (II)chloride complex (X)

Type of vibration	Frequencies in cm^{-1}	
	Compound (II)	Compound (X)
N-H stretching	3320	3320
Aryl C-H stretching	3140	3140
CH3 stretching	2950	2950
C=C	1500	1520
-CS-NH-	1330	1320
-CSNH-	1260	1260
-CSNH-	1230	1240
-CSNH-	1210	1210
C=S	1110	1110
C=CH	920	920
C=CH	760	760
C=CH	740	740
C=CH	640	720

H'nmr of the 3:3'-dichlorothiocarbanilide (spectrum 1a and 1b) is clear and acceptable, but the H'nmr of the 3:3'-dichlorothiocarbanilide.$MnCl_2$ complex (spectrum 2 and 3) is blurred.

The mass spectrum of 3:3'-dichlorothiocarbanilide.$MnCl_2$ complex gave an accurate m/z, m/z less Cl and m/z less 2Cls (Figures 2, 3 and 4).

From the point that sulphur is the more basic than nitrogen (more donar), and C=S was affected, we conclude that the donation is from sulphur more than nitrogen, and the proposed structure of 3:3'-dichlorothiocarbanilide.$MnCl_2$ complex (VIII) may be as follows



The same inner sphere complex structure could stand for compound (IX) and (X).

The substituent effect of the chlorine in meta-position in compound (VIII) and the meta-methyl in compound (IX) gave comparable percentage yield. This result is probably due to the fact that both chlorine atom and the methyl group have polarizibility effects (mesomeric and inductomeric). These polarization effects whatever their direction , reduce the energy of the system and so stabilize it[44].Besides steric hidrance might have reduced more the yield in compound (X).In the transition state the advent of the reagent brings new forces on the total system, and as this polarizable redistribution of electrons arise that will bring difference in the transition state derived from the unsubstituted and substituted thiocarbanilide.

CONCLUSION

The organometallic complexes of substituted thiocarbanilide – using manganese (II) chloride, which were prepared in our subject are unstable, inner sphere complexes.

We conclude that substituted thiocarbanilides can be used as analytical reagent for separation of manganese or manganese halides in acidic aqueous media.

Since gold salt and copper salt of thiocarbanilide have antituberculous activity, and although copper complexes of thiocarbanilides has an antiphenoloxidase activity, therefore our complexes must have biological activity.

REFERENCES

(1.) C. Dorothy Schroeder, Chem. Rev. 55, 182-188 (1955)

(2.) Chem. Abs. Vol. 49, 4442h (1955)

(3.) Chem. Abs. Vol. 50, 106 b(1956)

(4.) Chem. Abs. Vol. 64, 2738 a (1966)

(5.) T. Sugimura and Y. Minoura: Journal of Polymer science: part A-1, Vol. 4, 2735 (1966).

(6.) Chem. Abs. Vol. 49, 9296 d (1955).

(7.) Chem. Abs. Vol. 50, 8189 (1956).

(8.) P. J. Hanzlik and A. Irvine: J. Pharmacology, 17, 349 (1921).

(9) Maryl. Willard and Margaret Z. Jones; J. Am. Chem. Soc. 62, 2876-7 (1940).

(10) C. Dorothy Schroeder. Chem. Rev. 55, 189-99 (1955).

(11) T. C. Richard LOH and M. William Debn; J. Am. Chem. Soc. 48, 2956-9 (1926).

(12) Chem. Abs. Vol. 54, 16411 g (1960).

(13) A. David Zatko and Byron Kratochvil; Anal. Chem., 40 (14), 2120-3 (1968).

(14) M. Dehn William; J. Am. Chem. Soc., 62, 3189-90 (1940).

(15) Chem. Abs. Vol. 53, 21427 f (1959).

(16) Chem. Abs .Vol. 59, 8341 (1963).

(17) Chem. Abs. Vol. 20, 1081 (1926).

(18) Chem. Abs . Vol. 21, 92 (1927).

(19) S.Klare Markley and E. Emmett Reid; J. Am. Chem. Soc., 52, 2137-41 (1930).

(20) Chem. Abs. Vol. 47, 2707 a (1953).

(21) Chem. Abs. Vol. 43, 2021 c (1949).

(22) Chem. Abs. Vol. 43, 3003 (1949).

(23) Chem. Abs Vol. 49, 8989 i (1955).

(24) Chem. Abs. Vol. 41, 4003 f (1947).

(25) Chem. Abs. Vol. 40, 4310 (1946).

(26) Chem. Abs. Vol. 27, 1629 (1933).

(27) Ernst Bergmann and A. Weizmann; Transactions of the Faraday society, 34, 787-9 (1938).

(28) Chem. Abs. Vol. 53, 3883 a (1959).

(29) Chem. Abs. Vol. 68, 110907 a (1968).

(30) Chem. Abs. Vol. 45, 1529 i (1951).

(31) K. R. Bhaskar, R. K. Gosavi and C. N. R. Rao: Transactions of the Faraday society, 62, 29-38 (1960).

(32) Roy Kari and N. R. Kunchur; Canadian Journal of Chemistry, Vol., 42, 2628-9 (1964).

(33) P. A. Vaughn and J. Danahae; Acta Cryst. 5, 530 (1952).

(34) Chem. Abs. Vol. 66, 72241 g (1967).

(35) A. R. Amnathan, K. Sivakumar, K. Subramanian, N. Janarthanan, K. Ramadas, H. K. Fun; Acta Crystallographica section C:Crystal structure Communications, 52: part 1, 134-136 (1996).

(36) Chem. Abs. Vol. 49, 1974 d (1955).

(37) Chem. Abs. Vol. 53, 4542 d (1959).

(38) Chem. Abs. Vol. 52, 17599 h (1938).

(39) L. Karel, J. Pharmacol. Exptl. Therap. 93 (1948).

(40) I. Vogel; Pratical Organic Chemistry, third edition, 642 (1956).

(41) Chem. Abs. Vol. 21, 67 (1927).

(42) Frederick George Mann and Bernard Charles Sauders; Practical organic Chemistry, third edition, 395 (1952).

(43) I. Vogel; Elementry Practical Organic Chemistry, part 2: Qualitative Organic Analysis; Second edition, 31(1966).

(44) P.B.D. De La Mare and J. H. Ridd; Aromatic Substitution; 20 (1959).