Chapter 6.

PHYSICAL, CHEMICAL AND THERMAL STUDIES OF G-6 METAL CARBONYL DERIVATIVES OF 3,5-ALKYL/ARYL SUBSTITUTED-TETRAHYDRO-2H-1,3,5-THIAZIAINE-2-THIONE (DTTT)

Abstract

Fifteen new complexes, [M(CO)₄(L)₂] [M=Cr; Mo; W]; [L= met-DTTT; eth-DTTT; n-pr-DTTT; ph-DTTT and benz-DTTT] have been synthesized by the photochemical exchange reaction of [(η²⁻²-NBD)M(CO)₄] (M= Cr, Mo and W) with 3,5-dimethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (met-DTTT), 3,5-diethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (eth-DTTT), 3,5-di-n-propyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (n-pr-DTTT), 3,5-diphenyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (ph-DTTT), 3,5-dibenzyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (benz-DTTT). The new complexes have been characterized by elemental analysis, FTIR, ¹H NMR spectroscopy. The spectroscopic studies show that DTTT behaves as a monodentate ligand coordinating via the sulfur (C=S) donor atom.
6.1 Introduction

Dazomet (3,5-dimethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione or met-DTTT) is the fumigant or pesticide currently used to control soil fungi in both the conifer and shrub seedbeds. Control of soil-borne fungi, especially those which cause damping-off, has been good [1, 2]. Soil fumigants are pesticides that form gases when applied to soil. Once in the soil, the fumigants work by controlling pests that can disrupt plant growth and crop production. Soil fumigants play a very important role in agriculture, but they also have the potential to pose risk concerns to people (like handlers, workers and bystanders). Soil fumigation can provide benefits to both food consumers and growers. The magnitude of benefits depends on pest pressure, which varies over space and time, and the availability and costs associated with the use of alternatives [3]. Dazomet is applied before the planting of crops by soil incorporation, thereby causing it to act as a soil fumigant and disinfectant by decomposing to methyl isothiocyanate. It controls soil fungi (i.e. *Fusarium*, *Pythium*, *Rhizoctonia*, *Sclerotinia*, *Verticillium* and *Colletotrichum*), nematodes, germinating weed seeds and soil-dwelling insects [4].

In agriculture DTTT has found application as fungicide, herbicide and nematocide for cabbage, cucumber, maize, potato and tomato plants. In industrial environments DTTT has been used as slimicide in paper mills as a biocide in metal working fluids used in the manufacture of engines, transmissions, aircraft and specially metal products. The chemical DTTT has also been considered for use as a biocide in pump spray-delivered consumer products and custodial supplies. Respiratory exposure may occur from liquid aerosol generated during spray application of materials containing DTTT. Perhaps of a greater significance is the potential for exposure to volatile and semivolatile degradation products of DTTT. This ‘CS₂’ incorporated heterocycle is sparingly soluble in water and it has been equivocally proposed to undergo decomposition to formaldehyde, methylisothiocyanate and other compounds in aqueous solution [5-13]. It has been reported that DTTT gave unstable complexes with Cu(II), Co(II), Ni(II), Fe(III) ions in solution and were not isolated in solid form [14]. Sulfide carbonyl compounds continue to attract considerable attention not only on account of their fascinating structural chemistry, but also because of their ability to act as electron reservoirs and their potential in catalysis [15]. Features of the chemistry of these molecules which are currently of interest include the mechanisms and sites of substitution as well as the modification of reactivity accompanying carbonyl replacement by donor ligands [16]. Complexes [M(CO)₅(DTTT)] [M=Cr, Mo, W], Re(CO)₄Br(DTTT) and [Mn(CO)₂Cp(DTTT)] have been reported[17]. NBD (η²:2-norbornadiene) forms
organometallic complexes, where it can act as a two-electron or four-electron donor. Sandwiched compounds such as tetracarbonyl (η\(^{2,2}\)-norbornadiene) chromium (0), which is a useful reagent for transferring chromium tetracarbonyl to bidentate phosphine ligands, are known [18] 1,5-cyclooctadiene is also the starting material for the synthesis of diamantine and sumanene and it is used as an acetylene transfer agent for instance in reaction with 3,6-di-2-pyridyl-1,2,4,5-tetrazine [19]. The thermal substitution of Mo(CO)\(_4\)(η\(^{2,2}\)-COD) and Mo(CO)\(_4\)(η\(^{2,2}\)-NBD) with BFEDA gave the same product which was isolated by using the same procedure. Thus, both of Mo(CO)\(_4\)(η\(^{2,2}\)-NBD) and of Mo(CO)\(_4\)(η\(^{2,2}\)-COD) can be used as Mo(CO)\(_4\) transfer reagent for the synthesis of of Mo(CO)\(_4\)(BFEDA)[20, 21]. These literatures prompted us to study the behavior of (η\(^{2,2}\)-NBD)M(CO)\(_4\) as transfer reagent in G-6 metal carbonyl complexes.

In this chapter we have used five ligands (I) namely 3,5-dimethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (met-DTTT), 3,5-diethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (eth-DTTT), 3,5-di-n-propyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (n-pr-DTTT), 3,5-diphenyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (ph-DTTT), 3,5-dibenzyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (benz-DTTT) as ligands with M(CO)\(_4\)(η\(^{2,2}\)-NBD) (where M=Cr, Mo and W). M(CO)\(_4\)(η\(^{2,2}\)-NBD) was utilized as M(CO)\(_4\) transfer reagent.

In this paper, we report a noble photochemical route to the hitherto unknown fifteen new complexes (1a-3e). The complexes were characterized by elemental analysis, FT-IR, \(^1\)H-NMR spectroscopy. According to this the ligands(a-e) coordinates to the metal via (C=S) sulfur donor atom in (1a-3e). The spectroscopic studies suggest monodentate coordination of ligands in {M(CO)\(_4\)(met-DTTT)\(_2\)}(1a-3a); {M(CO)\(_4\)(eth-DTTT)\(_2\)}(1b-3b); {M(CO)\(_4\)(n-pr-DTTT)\(_2\)} (1c-3c); {M(CO)\(_4\)(ph-DTTT)\(_2\)} (1d-3d) and {M(CO)\(_4\)(benz-DTTT)\(_2\)} (1e-3e); where (M=Cr, Mo and W).

\[
\text{R} \quad \text{N} \quad \text{S} \quad \text{N} \quad \text{R} \\
\text{S} \quad \text{N} \quad \text{S}
\]

\[\text{a. (met-DTTT; R=CH}_3\text{)}; \text{ b. (eth-DTTT; R=C}_2\text{H}_5\text{)}; \text{ c. (n-pr-DTTT; R=C}_3\text{H}_7\text{)}; \]
\[\text{d. (ph-DTTT; R=C}_6\text{H}_5\text{)} \text{ and e. (benz-DTTT; R=C}_6\text{H}_5\text{CH}_2\text{)} \]

(I)
6.2 Experimental

Reactions were carried out under dry argon or in vacuo. All solvents were dried and degassed prior to use. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer (Model-577) in KBr discs and CH$_2$Cl$_2$. All the melting points were determined in an open capillary and are uncorrected. All glassware was oven dried at 120°C, molecular weight of the complexes were determined cryoscopically in benzene. Dichloromethane, 2,5-norbornadiene ($\eta^{2}$- NBD), n-hexane, n-pentane, benzene, methyl amine hydrochloride, formaldehyde, carbon disulfide, triethyl amine and iso-octane were purchased from E. Merck, while M(CO)$_6$ (M = Cr, Mo, W), 3,5-diethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (eth-DTTT), 3,5-di-n-propyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (n-pr-DTTT), 3,5-diphenyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (ph-DTTT), 3,5-dibenzyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (benz-DTTT) were purchased from Aldrich and were used as supplied.

Magnetic susceptibility measurements of the complexes were carried out by Gouy method. UV irradiation were performed with a medium pressure 400W mercury lamp through a quartz bulb.

6.2.1 Synthesis of Ligands

The ligand 3,5-dimethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (met-DTTT) was prepared as described in the literature [22]. Other ligands were purchased from Aldrich and used as supplied.

6.2.1.1 Synthesis of the 3,5-dimethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (met-DTTT)

**Synthesis:** A solution of CH$_3$NH$_2$.HCl (5.0g, 73mmol) in water (6 mL) and triethylamine (8.62g, 86mmol) was stirred for 10 min, and then CS$_2$ (2.84g, 38mmol) was added drop wise at room temperature with stirring for 20 min. Formaldehyde (2.30g, 76mmol) was added drop wise to the above reaction mixture, which was stirred for 30min until a white precipitate formed. met-DTTT was obtained as white solid by filtration. Yield, 80%. The complex was characterized and identified by means of IR and $^1$H-NMR spectroscopy. IR (in CH$_2$Cl$_2$): $\nu_{\text{sym}}$(C=S) 655 cm$^{-1}$, $\nu_{\text{as}}$(C=S) 600 cm$^{-1}$, $^1$H-NMR (in CDCl$_3$) $\delta$= 2.46 (s, 3H, 5-CH$_3$), 3.30 (s, 3H, 3-CH$_3$), 1.27 (s, 2H, 2-CH$_2$), 6.34 (s, 2H, 4-CH$_2$).

**Solubility:** Freely soluble in water, alcohol, n-pentane and chloroform.
6.2.2 Synthesis of the M(CO)₄(bicyclo[2.1.1] hepta-2,5-diene) or M(CO)₄(η²:²-NBD) -

Mo(CO)₄(η²:²-NBD), Cr(CO)₄(η²:²-NBD) and W(CO)₄(η²:²- NBD) were prepared following the method described in the literature [23, 24]. The preparation of Tetracarbonyl (η²:²- NBD) metal(0) is typical and is given here.

6.2.2.1 Preparation of Tetracarbonyl (η²:²-NBD)chromium(0)

**Synthesis:** Tetracarbonyl (η²:²- NBD)chromium(0), was prepared by refluxing 0.44g (2mmol) Cr(CO)₆ and 0.18g (2mmol) 2,5-norbornadiene (η²:²- NBD) in 25ml iso-octane. The reaction solution was evaporated to dryness. Crystallization from n-hexane solution yields yellow crystals of the complex.

**Solubility:** Freely soluble in DMF and DMSO and insoluble in methanol, nitrobenzene, dioxane and water.

6.2.2.2 Preparation of Tetracarbonyl (η²:²-NBD)molybdenum(0)

**Synthesis:** Tetracarbonyl (η²:²- NBD)molybdenum(0), was prepared by refluxing 0.63g (2mmol) Mo(CO)₆ and 0.18g (2mmol) 2,5-norbornadiene (η²:²- NBD) in 25ml iso-octane. The reaction solution was evaporated to dryness. Crystallization from n-hexane solution yields yellow crystals of the complex. The solvent was decanted and crystals were dried in vacuum.

**Solubility:** Freely soluble in DMF and DMSO and insoluble in methanol, nitrobenzene, dioxane and water.

6.2.2.3 Preparation of Tetracarbonyl (η²:²-NBD)tungsten(0)

**Synthesis:** Tetracarbonyl (η²:²-NBD)tungsten(0), was prepared by refluxing 0.94g (2mmol) W(CO)₆ and 0.18g (2mmol) 2,5-norbornadiene (η²:²- NBD) in 25ml iso-octane. The reaction solution was evaporated to dryness. Crystallization from n-hexane solution yields yellow crystals of the complex. The solvent was decanted and crystals were dried in vacuum.

**Solubility:** Freely soluble in DMF and DMSO and insoluble in methanol, nitrobenzene, dioxane and water.

6.2.3 Preparation of (L)₂M(CO)₄ complexes

The complexes (L)₂M(CO)₄ were prepared by exchange reaction of [(η²:²-NBD)M(CO)₄] with ligands (L).

6.2.3.1 Preparation of (met-DTTT)₂Cr(CO)₄ complex from exchange reaction of [(η²:²-NBD)Cr(CO)₄] (1a)
Synthesis: 0.384 g (1.5 mmol) sample of norbornadienetetracarbonylchromium [(\(\eta^{2:2}\)-NBD)Cr(CO)\(_4\)] was dissolved in 25mL of n-pentane. Then 0.486 g (3 mmol) of met-DTTT was added to the above solution with constant stirring. The mixture was irradiated for 10h. During the irradiation, the color of reaction mixture changed from off-white to dark yellow. After the irradiation the reaction mixture was evaporated under vacuum yielding a deep yellow solid. The solid residue was then washed with n-hexane so as to remove any [(\(\eta^{2:2}\)-NBD)Cr(CO)\(_4\)], \(\eta^{2:2}\)-NBD ligand itself, and other n-hexane soluble impurities. The deep yellow residue or remnant was dissolved in 1:1 CH\(_2\)Cl\(_2\)/n-hexane solution for recrystallization. Yellow microcrystal of [Cr(CO)\(_4\)(met-DTTT)]\(_2\) were obtained after waiting 24h at \(-15^\circ\text{C}\). Yield 75%.

Solubility: Freely soluble in DMF and DMSO and insoluble in methanol, nitrobenzene, dioxane and water.

6.2.3.2 Preparation of (met-DTTT)\(_2\)Mo(CO)\(_4\) complex from exchange reaction of [(\(\eta^{2:2}\)-NBD)Mo(CO)\(_4\)] (2a)

Synthesis: 0.528 g (1.5 mmol) sample of norbornadienetetracarbonylmolybdenum [(\(\eta^{2:2}\)-NBD)Mo(CO)\(_4\)] was dissolved in 25mL of n-pentane. Then 0.486 g (3 mmol) of met-DTTT was added to the above solution with constant stirring. The mixture was irradiated for 10h. During the irradiation, the color of reaction mixture changed from off-white to dark yellow. After the irradiation the reaction mixture was evaporated under vacuum yielding a deep yellow solid. The solid residue was then washed with n-hexane so as to remove any [(\(\eta^{2:2}\)-NBD)Mo(CO)\(_4\)], \(\eta^{2:2}\)-NBD ligand itself, and other n-hexane soluble impurities. The deep yellow residue or remnant was dissolved in 1:1 CH\(_2\)Cl\(_2\)/n-hexane solution for recrystallization. Yellow microcrystal of [Mo(CO)\(_4\)(met-DTTT)]\(_2\) were obtained after waiting 24h at \(-15^\circ\text{C}\). Yield 71%.

Solubility: Freely soluble in DMF and DMSO and insoluble in methanol, nitrobenzene, dioxane and water.

6.2.3.3 Preparation of (met-DTTT)\(_2\)W(CO)\(_4\) complex from exchange reaction of [(\(\eta^{2:2}\)-NBD)W(CO)\(_4\)] (3a)

Synthesis: 0.803 g (1.5 mmol) sample of norbornadienetetracarbonyltungsten [(\(\eta^{2:2}\)-NBD)W(CO)\(_4\)] was dissolved in 25mL of n-pentane. Then 0.486 g (3 mmol) of met-DTTT was added to the above solution with constant stirring. The mixture was irradiated for 10h. During the irradiation, the color of reaction mixture changed from off-white to dark yellow. After the irradiation the reaction mixture was evaporated under vacuum yielding a deep yellow solid. The solid residue was then washed with n-hexane so as to remove any [(\(\eta^{2:2}\)-
NBD)W(CO)$_4$, η$^{2:2}$- NBD ligand itself, and other n-hexane soluble impurities. The deep yellow residue or remnant was dissolved in 1:1 CH$_2$Cl$_2$/n-hexane solution for recrystallization. Yellow microcrystal of [W(CO)$_4$(met-DTTT)$_2$] were obtained after waiting 24h at –15°C. **Yield- 67%**.

**Solubility:** Freely soluble in DMF and DMSO and insoluble in methanol, nitrobenzene, dioxane and water.

### 6.2.3.4 Preparation of (eth-DTTT)$_2$Cr(CO)$_4$ complex from exchange reaction of [(η$^{2:2}$- NBD)Cr(CO)$_4$] (1b)

**Synthesis:** 0.384g (1.5 mmol) sample of norbornadienetetracarbonylchromium [(η$^{2:2}$- NBD)Cr(CO)$_4$] was dissolved in 25mL of n-pentane. Then 0.570 g (3 mmol) of eth-DTTT was added to the above solution with constant stirring. The mixture was irradiated for 10h. During the irradiation, the color of reaction mixture changed from off-white to dark yellow. After the irradiation the reaction mixture was evaporated under vacuum yielding a deep yellow solid. The solid residue was then washed with n-hexane so as to remove any [(η$^{2:2}$- NBD)Cr(CO)$_4$], η$^{2:2}$- NBD ligand itself, and other n-hexane soluble impurities. The deep yellow residue or remnant was dissolved in 1:1 CH$_2$Cl$_2$/n-hexane solution for recrystallization. Yellow microcrystal of [Cr(CO)$_4$(eth-DTTT)$_2$] were obtained after waiting 24h at –15°C. **Yield- 73%**.

**Solubility:** Freely soluble in DMF and DMSO and insoluble in methanol, nitrobenzene, dioxane and water.

### 6.2.3.5 Preparation of (eth-DTTT)$_2$Mo(CO)$_4$ complex from exchange reaction of [(η$^{2:2}$- NBD)Mo(CO)$_4$] (2b)

**Synthesis:** 0.528g (1.5 mmol) sample of norbornadienetetracarbonylmolybdenum [(η$^{2:2}$- NBD)Mo(CO)$_4$] was dissolved in 25mL of n-pentane. Then 0.570 g (3 mmol) of eth-DTTT was added to the above solution with constant stirring. The mixture was irradiated for 10h. During the irradiation, the color of reaction mixture changed from off-white to dark yellow. After the irradiation the reaction mixture was evaporated under vacuum yielding a deep yellow solid. The solid residue was then washed with n-hexane so as to remove any [(η$^{2:2}$- NBD)Mo(CO)$_4$], η$^{2:2}$- NBD ligand itself, and other n-hexane soluble impurities. The deep yellow residue or remnant was dissolved in 1:1 CH$_2$Cl$_2$/n-hexane solution for recrystallization. Yellow microcrystal of [Mo(CO)$_4$(eth-DTTT)$_2$] were obtained after waiting 24h at –15°C. **Yield- 74%**.

**Solubility:** Freely soluble in DMF and DMSO and insoluble in methanol, nitrobenzene, dioxane and water.
6.2.3.6 Preparation of (eth-DTTT)$_2$W(CO)$_4$ complex from exchange reaction of [(η$^{2\text{-2}}$-NBD)W(CO)$_4$] (3b)

**Synthesis:** 0.803g (1.5 mmol) sample of norbornadienetetracarbonyltungsten [(η$^{2\text{-2}}$-NBD)W(CO)$_4$] was dissolved in 25mL of n-pentane. Then 0.570 g (3 mmol) of eth-DTTT was added to the above solution with constant stirring. The mixture was irradiated for 10h. During the irradiation, the color of reaction mixture changed from off-white to dark yellow. After the irradiation the reaction mixture was evaporated under vacuum yielding a deep yellow solid. The solid residue was then washed with n-hexane so as to remove any [(η$^{2\text{-2}}$-NBD)W(CO)$_4$], η$^{2\text{-2}}$- NBD ligand itself, and other n-hexane soluble impurities. The deep yellow residue or remnant was dissolved in 1:1 CH$_2$Cl$_2$/n-hexane solution for recrystallization. Yellow microcrystal of [W(CO)$_4$(eth-DTTT)$_2$] were obtained after waiting 24h at −15°C. **Yield- 68%**.

**Solubility:** Freely soluble in DMF and DMSO and insoluble in methanol, nitrobenzene, dioxane and water.

6.2.3.7 Preparation of (n-pr-DTTT)$_2$Cr(CO)$_4$ complex from exchange reaction of [(η$^{2\text{-2}}$-NBD)Cr(CO)$_4$] (1c)

**Synthesis:** 0.384g (1.5 mmol) sample of norbornadienetetracarbonylchromium [(η$^{2\text{-2}}$-NBD)Cr(CO)$_4$] was dissolved in 25mL of n-pentane. Then 0.654 g (3 mmol) of n-pr-DTTT was added to the above solution with constant stirring. The mixture was irradiated for 10h. During the irradiation, the color of reaction mixture changed from off-white to dark yellow. After the irradiation the reaction mixture was evaporated under vacuum yielding a deep yellow solid. The solid residue was then washed with n-hexane so as to remove any [(η$^{2\text{-2}}$-NBD)Cr(CO)$_4$], η$^{2\text{-2}}$- NBD ligand itself, and other n-hexane soluble impurities. The deep yellow residue or remnant was dissolved in 1:1 CH$_2$Cl$_2$/n-hexane solution for recrystallization. Yellow microcrystal of [Cr(CO)$_4$(n-pr-DTTT)$_2$] were obtained after waiting 24h at −15°C. **Yield- 72%**.

**Solubility:** Freely soluble in DMF and DMSO and insoluble in methanol, nitrobenzene, dioxane and water.

6.2.3.8 Preparation of (n-pr-DTTT)$_2$Mo(CO)$_4$ complex from exchange reaction of [(η$^{2\text{-2}}$-NBD)Mo(CO)$_4$] (2c)

**Synthesis:** 0.53g (1.5 mmol) sample of norbornadienetetracarbonylmolybdenum [(η$^{2\text{-2}}$-NBD)Mo(CO)$_4$] was dissolved in 25mL of n-pentane. Then 0.654 g (3 mmol) of n-pr-DTTT was added to the above solution with constant stirring. The mixture was irradiated for 10h.
During the irradiation, the color of reaction mixture changed from off-white to dark yellow. After the irradiation the reaction mixture was evaporated under vacuum yielding a deep yellow solid. The solid residue was then washed with n-hexane so as to remove any \([\eta^{2:2}\text{-NBD}]\text{Mo(CO)}_4\), \(\eta^{2:2}\text{-NBD}\) ligand itself, and other n-hexane soluble impurities. The deep yellow residue or remnant was dissolved in 1:1 CH\(_2\)Cl\(_2\)/n-hexane solution for recrystallization. Yellow microcrystal of [Mo(CO\(_4\))(n-pr-DTTT)\(_2\)] were obtained after waiting 24h at −15°C. **Yield- 73\%**.

**Solubility:** Freely soluble in DMF and DMSO and insoluble in methanol, nitrobenzene, dioxane and water.

### 6.2.3.9 Preparation of \((n\text{-pr-DTTT})_2\text{W(CO)}_4\) complex from exchange reaction of \([\eta^{2:2}\text{-NBD}]\text{W(CO)}_4\) (3c)

**Synthesis:** 0.803g (1.5 mmol) sample of norbornadienetetracarbonyltungsten \([\eta^{2:2}\text{-NBD}]\text{W(CO)}_4\) was dissolved in 25mL of n-pentane. Then 0.654 g (3 mmol) of n-pr-DTTT was added to the above solution with constant stirring. The mixture was irradiated for 10h. During the irradiation, the color of reaction mixture changed from off-white to dark yellow. After the irradiation the reaction mixture was evaporated under vacuum yielding a deep yellow solid. The solid residue was then washed with n-hexane so as to remove any \([\eta^{2:2}\text{-NBD}]\text{W(CO)}_4\), \(\eta^{2:2}\text{-NBD}\) ligand itself, and other n-hexane soluble impurities. The deep yellow residue or remnant was dissolved in 1:1 CH\(_2\)Cl\(_2\)/n-hexane solution for recrystallization. Yellow microcrystal of [W(CO\(_4\))(n-pr-DTTT)\(_2\)] were obtained after waiting 24h at −15°C. **Yield- 69\%**.

**Solubility:** Freely soluble in DMF and DMSO and insoluble in methanol, nitrobenzene, dioxane and water.

### 6.2.3.10 Preparation of \((ph\text{-DTTT})_2\text{Cr(CO)}_4\) complex from exchange reaction of \([\eta^{2:2}\text{-NBD}]\text{Cr(CO)}_4\) (1d)

**Synthesis:** 0.384g (1.5 mmol) sample of norbornadienetetracarbonylchromium \([\eta^{2:2}\text{-NBD}]\text{Cr(CO)}_4\) was dissolved in 25mL of n-pentane. Then 0.858 g (3 mmol) of ph-DTTT was added to the above solution with constant stirring. The mixture was irradiated for 10h. During the irradiation, the color of reaction mixture changed from off-white to dark yellow. After the irradiation the reaction mixture was evaporated under vacuum yielding a deep yellow solid. The solid residue was then washed with n-hexane so as to remove any \([\eta^{2:2}\text{-NBD}]\text{Cr(CO)}_4\), \(\eta^{2:2}\text{-NBD}\) ligand itself, and other n-hexane soluble impurities. The deep yellow residue or remnant was dissolved in 1:1 CH\(_2\)Cl\(_2\)/n-hexane solution for
recrystallization. Yellow microcrystal of [Cr(CO)$_4$(ph-DTTT)$_2$] were obtained after waiting 24h at –15°C. Yield 70%.

**Solubility:** Freely soluble in DMF and DMSO and insoluble in methanol, nitrobenzene, dioxane and water.

### 6.2.3.11 Preparation of (n-pr-DTTT)$_2$Mo(CO)$_4$ complex from exchange reaction of [($\eta^{2:2}$- NBD)Mo(CO)$_4$] (2d)

**Synthesis:** 0.528g (1.5 mmol) sample of norbornadienetetracarbonylmolybdenum [(($\eta^{2:2}$- NBD)Mo(CO)$_4$] was dissolved in 25mL of n-pentane. Then 0.858 g (3 mmol) of ph-DTTT was added to the above solution with constant stirring. The mixture was irradiated for 10h. During the irradiation, the color of reaction mixture changed from off-white to dark yellow. After the irradiation the reaction mixture was evaporated under vacuum yielding a deep yellow solid. The solid residue was then washed with n-hexane so as to remove any [(($\eta^{2:2}$- NBD)Mo(CO)$_4$], $\eta^{2:2}$- NBD ligand itself, and other n-hexane soluble impurities. The deep yellow residue or remnant was dissolved in 1:1 CH$_2$Cl$_2$/n-hexane solution for recrystallization. Yellow microcrystal of [Mo(CO)$_4$(ph-DTTT)$_2$] were obtained after waiting 24h at –15°C. Yield 72%.

**Solubility:** Freely soluble in DMF and DMSO and insoluble in methanol, nitrobenzene, dioxane and water.

### 6.2.3.12 Preparation of (ph-DTTT)$_2$W(CO)$_4$ complex from exchange reaction of [($\eta^{2:2}$- NBD)W(CO)$_4$] (3d)

**Synthesis:** 0.803g (1.5 mmol) sample of norbornadienetetracarbonyltungsten [(($\eta^{2:2}$- NBD)W(CO)$_4$] was dissolved in 25mL of n-pentane. Then 0.858 g (3 mmol) of ph-DTTT was added to the above solution with constant stirring. The mixture was irradiated for 10h. During the irradiation, the color of reaction mixture changed from off-white to dark yellow. After the irradiation the reaction mixture was evaporated under vacuum yielding a deep yellow solid. The solid residue was then washed with n-hexane so as to remove any [(($\eta^{2:2}$- NBD)W(CO)$_4$], $\eta^{2:2}$- NBD ligand itself, and other n-hexane soluble impurities. The deep yellow residue or remnant was dissolved in 1:1 CH$_2$Cl$_2$/n-hexane solution for recrystallization. Yellow microcrystal of [W(CO)$_4$(ph-DTTT)$_2$] were obtained after waiting 24h at –15°C. Yield 66%.

**Solubility:** Freely soluble in DMF and DMSO and insoluble in methanol, nitrobenzene, dioxane and water.
6.2.3.13 Preparation of (benz-DTTT)$_2$Cr(CO)$_4$ complex from exchange reaction of [(η$^{2:2}$-NBD)Cr(CO)$_4$] (1e)

**Synthesis:** 0.384g (1.5 mmol) sample of norbornadienetetracarbonylchromium [(η$^{2:2}$-NBD)Cr(CO)$_4$] was dissolved in 25mL of n-pentane. Then 0.942 g (3 mmol) of benz-DTTT was added to the above solution with constant stirring. The mixture was irradiated for 10h. During the irradiation, the color of reaction mixture changed from off-white to dark yellow. After the irradiation the reaction mixture was evaporated under vacuum yielding a deep yellow solid. The solid residue was then washed with n-hexane so as to remove any [(η$^{2:2}$-NBD)Cr(CO)$_4$], η$^{2:2}$-NBD ligand itself, and other n-hexane soluble impurities. The deep yellow residue or remnant was dissolved in 1:1 CH$_2$Cl$_2$/n-hexane solution for recrystallization. Yellow microcrystal of [Cr(CO)$_4$(benz-DTTT)$_2$] were obtained after waiting 24h at −15°C. **Yield- 76%**.

**Solubility:** Freely soluble in DMF and DMSO and insoluble in methanol, nitrobenzene, dioxane and water.

6.2.3.14 Preparation of (benz-DTTT)$_2$Mo(CO)$_4$ complex from exchange reaction of [(η$^{2:2}$-NBD)Mo(CO)$_4$] (2d)

**Synthesis:** 0.528g (1.5 mmol) sample of norbornadienetetracarbonylmolybdenum [(η$^{2:2}$-NBD)Mo(CO)$_4$] was dissolved in 25mL of n-pentane. Then 0.942 g (3 mmol) of benz-DTTT was added to the above solution with constant stirring. The mixture was irradiated for 10h. During the irradiation, the color of reaction mixture changed from off-white to dark yellow. After the irradiation the reaction mixture was evaporated under vacuum yielding a deep yellow solid. The solid residue was then washed with n-hexane so as to remove any [(η$^{2:2}$-NBD)Mo(CO)$_4$], η$^{2:2}$-NBD ligand itself, and other n-hexane soluble impurities. The deep yellow residue or remnant was dissolved in 1:1 CH$_2$Cl$_2$/n-hexane solution for recrystallization. Yellow microcrystal of [Mo(CO)$_4$(benz-DTTT)$_2$] were obtained after waiting 24h at −15°C. **Yield- 74%**.

**Solubility:** Freely soluble in DMF and DMSO and insoluble in methanol, nitrobenzene, dioxane and water.

6.2.3.15 Preparation of (benz-DTTT)$_2$W(CO)$_4$ complex from exchange reaction of [(η$^{2:2}$-NBD)W(CO)$_4$] (3e)

**Synthesis:** 0.803g (1.5 mmol) sample of norbornadienetetracarbonyltungsten [(η$^{2:2}$-NBD)W(CO)$_4$] was dissolved in 25mL of n-pentane. Then 0.942 g (3 mmol) of benz-DTTT was added to the above solution with constant stirring. The mixture was irradiated for 10h.
During the irradiation, the color of reaction mixture changed from off-white to dark yellow. After the irradiation the reaction mixture was evaporated under vacuum yielding a deep yellow solid. The solid residue was then washed with n-hexane so as to remove any [(η\textsuperscript{2:2}-NBD)W(CO)\textsubscript{4}], η\textsuperscript{2:2}-NBD ligand itself, and other n-hexane soluble impurities. The deep yellow residue or remnant was dissolved in 1:1 CH\textsubscript{2}Cl\textsubscript{2}/n-hexane solution for recrystallization. Yellow microcrystal of [W(CO)\textsubscript{4}(benz-DTTT)\textsubscript{2}] were obtained after waiting 24h at –15°C. Yield - 70%.

**Solubility:** Freely soluble in DMF and DMSO and insoluble in methanol, nitrobenzene, dioxane and water.

**Scheme 1** – Thermal Reaction of η\textsuperscript{2:2}-NBD with M(CO)\textsubscript{6} (M = Cr, Mo, W)

![Scheme 1](image1)

**Scheme 2** – Ligand Substitution reaction of η\textsuperscript{2:2}-NBD in M(CO)\textsubscript{4}(η\textsuperscript{2:2}-NBD) with DTTT

![Scheme 2](image2)

(1): M=Cr; (2): M=Mo; (3): M=W;
(a): met-DTTT, R=CH\textsubscript{3}; (b): eth-DTTT, R=C\textsubscript{2}H\textsubscript{5}; (c): n-Pr-DTTT, R=C\textsubscript{3}H\textsubscript{7}; (d): ph-DTTT, R=C\textsubscript{6}H\textsubscript{5} and (e): benz-DTTT, R= C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}.

### 6.3 Results and Discussion

The transfer reagents Mo(CO)\textsubscript{4}(η\textsuperscript{2:2}-NBD), Cr(CO)\textsubscript{4}(η\textsuperscript{2:2}-NBD) and W(CO)\textsubscript{4}(η\textsuperscript{2:2}-NBD) were prepared by thermal reaction of 2,5-norbornadiene (NBD) with M(CO)\textsubscript{6} (M= Cr, Mo, W) according to Scheme-1. Complexes (1a-3e) were prepared by photochemical reaction as shown in Scheme-2. Analytical data for {M(CO)\textsubscript{4}(met-DTTT)\textsubscript{2}}(1a-3a); {M(CO)\textsubscript{4}(eth-DTTT)\textsubscript{2}}(1b-3b); {M(CO)\textsubscript{4}(n-pr-DTTT)\textsubscript{2}} (1c-3c); {M(CO)\textsubscript{4}(ph-DTTT)\textsubscript{2}} (1d-3d) and
The photogeneration of M(CO)$_5$ from M(CO)$_6$ (M=Cr, Mo & W) has been extensively studied. These 16-electron M(CO)$_5$ fragments react quickly with any available donor atom to yield a M(CO)$_5$L species; and where L is a chelating bidentate ligand, rapid continuation to the chelating M(CO)$_4$L or bridging M$_2$(CO)$_{10}$ (µ-L) products may occur [25-28]. The photochemical reactions of Mo(CO)$_4$(η$_2$-NBD) with DTTT proceed in an entirely expected manner by displacement of the NBD ligand to give the monometallic complexes (1a-3e).

In this study, photochemical reactions of M(CO)$_4$(NBD) (M=Cr, Mo & W) with met-DTTT (a); eth-DTTT (b); n-pr-DTTT (c); ph-DTTT (d) and benz-DTTT (e) ligands occurs in this expected manner, and gave hitherto a series of complexes (1a)-(1e); (2a)-(2e) and (3a)-(3e) occur via the displacement of NBD from M(CO)$_4$(NBD) (M=Cr, Mo & W) and coordination of metal atom via two Sulfur donor atoms (C=S) of two molecules of the ligand yielding cis-M(CO)$_4$L$_2$ complexes. Important IR spectral bands M(CO)$_4$L$_2$ (L = met-DTTT (a); eth-DTTT (b); n-pr-DTTT (c); ph-DTTT (d); benz-DTTT (e) and M=Cr, Mo & W) are presented in Table-6.3.

The evidence about the metal-sulfur (M–S) bond formation is the appearance of a new band in all the complexes around 385-403 cm$^{-1}$, which may be assigned to the ν(M–S) mode [29] can be correlated with the decrease in ν(CO) modes of (1a-3e) complexes move to lower wave numbers in comparison with the starting M(CO)$_6$ (M= Cr, Mo & W) molecules [30, 31]. This decrease in the frequency of CO absorption is because of the accumulation of charge density on metal atom (Cr, Mo and W) which stabilizes itself by transferring it back to the nearby CO (a π-acceptor ligand) [32].

Four bands in the range (2002-2020 cm$^{-1}$), (1851-1948 cm$^{-1}$), (1831-1910 cm$^{-1}$) and (1782-1853 cm$^{-1}$) arising from ν (CO) vibrations are seen which presumably have local c$_{2v}$ symmetry of M(CO)$_4$ unit in {M(CO)$_4$(met-DTTT)$_2$} (1a-3a); {M(CO)$_4$(eth-DTTT)$_2$} (1b-3b); {M(CO)$_4$(n-pr-DTTT)$_2$} (1c-3c); {M(CO)$_4$(ph-DTTT)$_2$} (1d-3d) and {M(CO)$_4$(benz-DTTT)$_2$} (1e-3e); where (M= Cr, Mo & W) complexes (Scheme-2). These values are in close resemblance to the values of ν (CO) vibration for other sulfur containing disubstituted group-6 metal carbonyls [33-36]. The presence of normal ligand bands indicated that these bands were intact in the complexes. The nature and number of CO bands indicated that these bands resemble closely to the bands of other known di and trisubstituted metal carbonyls [35, 37, 38].
The IR spectra data for (1a-3e) show a decrease in $v_{as}(C=S)$ on coordination. In the free ligand the IR active mode $v_{as}(C=S)$ is at 628 cm$^{-1}$ for met-DTTT [33]. On coordination, two bands are observed in the range 666-668 cm$^{-1}$ [$v_{sym}(C=S)$] and 607-610 cm$^{-1}$ [$v_{as}(C=S)$]; 660-670 cm$^{-1}$ [$v_{sym}(C=S)$] and 610-612 cm$^{-1}$ [$v_{as}(C=S)$]; 662-665 cm$^{-1}$ [$v_{sym}(C=S)$] and 615-618 cm$^{-1}$ [$v_{as}(C=S)$]; 664-672 cm$^{-1}$ [$v_{sym}(C=S)$] and 613-616 cm$^{-1}$ [$v_{as}(C=S)$] and 665-672 cm$^{-1}$ [$v_{sym}(C=S)$] and 616-622 cm$^{-1}$ [$v_{as}(C=S)$] in the case of met-DTTT, eth-DTTT, n-pr-DTTT, ph-DTTT and benz-DTTT respectively. As expected four bands arising from $v(CO)$ vibrations are seen for each complex which presumably have local $C_{2v}$ symmetry of the M(CO)$_4$ unit [39] and confirming the cis- complexes [40].

In addition, magnetic susceptibility measurement shows that (1a-3e) complexes were diamagnetic. Since these complexes have M(0) [M=Cr, Mo, W] with a low spin d$^6$ configuration. Such diamagnetism might arise from further splitting of the d-orbital in the low symmetry complexes i.e. $d_{xy}^2$, $d_{xz}^2$, $d_{yz}^2$, $d(x^2-y^2)^0$, $dz^2$ [41, 42].

**Antimicrobial activity**

All the synthesized complexes were screened for their antibacterial activity by using agar diffusion method [43] against *S. aureus*, *B. subtile* gram positive and *E. coli*, *S. paratyphi* gram negative bacteria in nutrient agar medium. Ciprofloxacin was used as standard drug for comparison. The antifungal activity of the synthesized compounds was tested *in vitro* against different strains of fungi using the standard agar disk diffusion method.

The ligand DTTT and their metal carbonyl complexes shows good antibacterial and antifungal activity. Results of the *in vitro* antifungal investigation revealed that metal carbonyl derivatives of met-DTTT(1a-3a) and eth-DTTT(1b-3b) exhibited antifungal activity against two strains of the tested fungi. At 100 mM ml$^{-1}$ concentration, significant growth inhibitory activity produced by metal carbonyl derivatives of n-pr-DTTT (1c-3c) on *C. albicans* and *F. oxysporum*, with inhibitory zones of 12 and 11mm respectively. Metal carbonyl derivatives of ph-DTTT (1d-3d) produced a fairly good antifungal activity against *C. albicans* with inhibitory zone of 7mm. Furthermore, at the lower concentration, 50 mM ml$^{-1}$, metal carbonyl derivatives of benz-DTTT (1e-3e) solely showed quite good activity against *F. oxysporum* with inhibitory zones of 8mm.

Metal carbonyl derivatives of met-DTTT(1a-3a) and eth-DTTT(1b-3b), revealed a significant bacterial growth inhibitory activity at 100 mM ml$^{-1}$ concentration with inhibitory
zones of 11 and 9 mm on both gram positive and gram negative bacteria. Metal carbonyl derivatives of n-pr-DTTT(1c-3c) shows moderate inhibitory activity against gram positive bacteria while metal carbonyl derivatives of ph-DTTT (1d-3d) and (1e-3e) were found almost ineffective against gram positive bacteria. All above derivatives were found sufficient inhibitory activity against gram negative bacteria.

6.4 Conclusion

The IR spectroscopic results show that the ligands (a-e) coordinate via sulfur (C=S) atom in (1a-3e) and these ligands behave as monodentate ligand. The IR data are well accord with cis- coordination of ligands. These results suggest that the ligands mainly acting a $\sigma$– donor. The obtained results show that DTTT and its metalcarbonyl derivatives exert a moderate inhibitory effect on different bacterial and fungal activity, thus confirming previous data.
Fig. 6.2 Structure Sheet of Ligands L [L= met-DTTT; eth-DTTT; n-pr-DTTT; ph-DTTT and benz-DTTT]

3,5-dimethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione
(met-DTTT)

Chemical Formula: C_5H_{10}N_2S_2
M.P. : 103.2 °C
Appearance : white solid
Abbreviation : a

3,5-diethyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione (eth-DTTT)

Chemical Formula: C_7H_{14}N_2S_2
M.P. : 103.5 °C
Appearance: white solid
Abbreviation : b

3,5-di-n-propyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione
(n-pr-DTTT)

Chemical Formula: C_9H_{18}N_2S_2
M.P. : 104 °C
Appearance : colorless needles
Abbreviation : c

3,5-diphenyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione
(ph-DTTT)

Chemical Formula: C_{15}H_{14}N_2S_2
M.P. : 105 °C
Appearance : colorless needles
Abbreviation : d
3,5-dibenzyl-tetrahydro-2H-1,3,5-thiadiazine-2-thione
(benz-DTTT)

**Fig. 6.3 Structure Sheet of Complexes (1a-3e)**

Chemical Formula: $C_{17}H_{18}N_2S_2$
M.P. : 105.2 °C
Appearance : colorless needles
Abbreviation : e

Chemical Formula: $C_{14}H_{20}CrO_4N_4S_4$
M.P. : 169 °C
Appearance : yellow solid
Abbreviation : (1a)

ChemicalFormula: $C_{14}H_{20}MoO_4N_4S_4$
M.P. : 173 °C
Appearance : yellow solid
Abbreviation : (2a)
Chemical Formula: $\text{C}_{14}\text{H}_{20}\text{WO}_{4}\text{N}_{4}\text{S}_{4}$
M.P.: 178 °C
Appearance: yellow colored solid
Abbreviation: (3a)

Chemical Formula: $\text{C}_{18}\text{H}_{28}\text{CrO}_{4}\text{N}_{4}\text{S}_{4}$
M.P.: 170 °C
Appearance: dark yellow solid
Abbreviation: (1b)

Chemical Formula: $\text{C}_{18}\text{H}_{28}\text{MoO}_{4}\text{N}_{4}\text{S}_{4}$
M.P.: 174 °C
Appearance: yellow solid
Abbreviation: (2b)
[W(CO)$_4$(eth-DTTT)$_2$]

Chemical Formula: C$_{18}$H$_{28}$WO$_4$N$_4$S$_4$
M.P.: 179 °C
Appearance: yellow colored solid
Abbreviation: (3b)

[Cr(CO)$_4$(n-pr-DTTT)$_2$]

Chemical Formula: C$_{22}$H$_{36}$CrO$_4$N$_4$S$_4$
M.P.: 171 °C
Appearance: dark yellow solid
Abbreviation: (1c)

[Mo(CO)$_4$(n-pr-DTTT)$_2$]

Chemical Formula: C$_{22}$H$_{36}$MoO$_4$N$_4$S$_4$
M.P.: 175 °C
Appearance: yellow solid
Abbreviation: (2c)
Chemical Formula: $\text{C}_{27}\text{H}_{36}\text{WO}_{4}\text{N}_{4}\text{S}_{4}$
M.P.: 180 °C
Appearance: yellow colored solid
Abbreviation: (3c)

Chemical Formula: $\text{C}_{34}\text{H}_{28}\text{CrO}_{4}\text{N}_{4}\text{S}_{4}$
M.P.: 168 °C
Appearance: dark yellow solid
Abbreviation: (1d)

Chemical Formula: $\text{C}_{34}\text{H}_{28}\text{MoO}_{4}\text{N}_{4}\text{S}_{4}$
M.P.: 172 °C
Appearance: yellow solid
Abbreviation: (2d)
Chemical Formula: C$_3$H$_{28}$WO$_4$N$_4$S$_4$
M.P. : 177 °C
Appearance : yellow colored solid
Abbreviation : (3d)

Chemical Formula: C$_{38}$H$_{36}$CrO$_4$N$_4$S$_4$
M.P. : 169 °C
Appearance : dark yellow solid
Abbreviation : (1e)
Chemical Formula: $\text{C}_{38}\text{H}_{36}\text{MoO}_4\text{N}_4\text{S}_4$
M.P. : 173 °C
Appearance : yellow solid
Abbreviation : (2e)

Chemical Formula: $\text{C}_{38}\text{H}_{36}\text{WO}_4\text{N}_4\text{S}_4$
M.P. : 178 °C
Appearance : yellow colored solid
Abbreviation : (3e)
6.5 References:


